For Reference

NOT TO BE TAKEN FROM THIS ROOM

Library of the University of Alberta, Edmonton, Alberta

Wanat, William.

EVALUATION OF THE PIDGEON PROCESS FOR THE MANUFACTURE OF CARBON BLACK FROM NATURAL GAS. Pt. 1. Design and construction of Pilot Plant equipment.

Dept. of Chemical and Petroleum Engineering. M.SC. 1951.

Ex libris
universitatis
albertaensis

THE UNIVERSITY OF ALBERTA

EVALUATION OF THE PIDGEON PROCESS FOR THE MANUFACTURE OF CARBON BLACK FROM NATURAL GAS

I. DESIGN AND CONSTRUCTION OF PILOT PLANT EQUIPMENT

A DISSERTATION
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE

FACULTY OF ENGINEERING
DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

by WILLIAM WANAT

EDMONTON, ALBERTA
October 1, 1951.

Digitized by the Internet Archive
in 2017 with funding from
University of Alberta Libraries

https://archive.org/details/evaluationofpidg00will

ACKNOWLEDGEMENT

Grateful acknowledgement is extended to all those who have assisted in this investigation:

To Dr. Donald Quon, for assistance in and supervision of the project,

To Dr. G. W. Govier, director of the project, whose assistance and advice were invaluable,

To Dr. D. B. Robinson, for assistance in the design of the equipment,

To the Research Council of Alberta who financed this project,

To the Consolidated Mining and Smelting Company of Canada, Ltd. for the Research Fellowship, which enabled the writer to carry on this investigation,

To the Department of Chemical and Petroleum Engineering for services and supplies.

THE PROBLEM

The general problem undertaken was an engineering and economic evaluation under Alberta conditions of the Pidgeon process (26) for the manufacture of carbon black from natural gas. Specifically, this investigation was to have dealt with:

(1) the design of equipment using commercial size refractory tubes

(2) the testing of the equipment design and materials of construction

(3) the collection of fundamental data on the gas phase decomposition of natural gas under controlled conditions

(4) evaluation of the carbon black produced

Due to the failure of the available refractory tubes, only the first two parts of the investigation were carried out.

TABLE OF CONTENTS

Page No.

The Problem

Table of Contents

List of Illustrations

Summary

Section I. Introduction 1

II. Fundamental Characteristics of Carbon Black 7

III. Carbon Black Processes 13

IV. The Pidgeon Process - A Review of Pidgeon's Work 21

V. Equipment Design 27

VI. Experimental Program 61

VII. Experimental Results and Discussion 65

VIII. General Discussion 70

Bibliography 73

Appendix A. Equipment Design Calculations - following page 75

B. Operating Technique viii

C. Equipment Construction Problems xii

D. Calculation of Heat Available from Off-Gas xix

E. Carbon Black Bibliography xxii

LIST OF FIGURES

		Page No.
Figure I.	Effect of time of contact on carbon black yield	25
II.	View of complete unit	28
III.	The furnace case	31
IV.	The furnace	34
V.	A view of the jet ejectors	35
VI.	Transverse cross section of the furnace	37
VII.	Longitudinal cross section of the furnace	38
VIII.	A view of the incomplete brickwork	39
IX.	The complete brickwork of the furnace	40
X.	Lighting ports and silicon carbide plate mounting	41
XI.	Flue gas quench unit	43
XII.	Flood warning system circuit	44
XIII.	Compressor installation	46
XIV.	Pyrometer port quartz window mounting	48
XV.	Off-gas quench unit	49
XVI.	Bag filter unit and off-gas quench unit	50
XVII.	Bag filter unit	51
XVIII.	Bag filter mounting	54
XIX.	Control panel	55
XX.	A view of the back of the control panel	56
XXI.	Schematic diagram of the complete unit	57

SUMMARY

This investigation involved the design and construction of pilot plant equipment for the engineering and economic evaluation of the Pidgeon Process for the manufacture of carbon black from natural gas.

The process, investigated on a laboratory scale by Dr. L. M. Pidgeon for the National Research Council in 1935 involves the thermal decomposition of natural gas in externally heated refractory tubes. The essential feature of the process is the use of permeable refractory tubes through the walls of which a certain amount of inert gas is allowed to pass. By this means the deposition of carbon black thereon is prevented. In the laboratory scale equipment yields as high as 19 pounds of good quality carbon black per thousand cubic feet of natural gas were obtained.

An extensive literature search was carried out to obtain information on equipment design, operating conditions and the fundamental characteristics of carbon black. These characteristics are: pH, surface area, structure, roughness factor and surface activity. The most important factors affecting these characteristics are reaction temperature and contact time at this temperature.

A furnace and auxiliary equipment designed for reactor tubes with an inside diameter up to 3 inches and a length of 4 feet, were built. Permeable aluminum oxide reactor tubes with inside diameters of 2 and 3 inches and wall thicknesses of

1/2 and 1/4 inches respectively were tested but no results were obtained due to the failure of the reactor tubes. Each of the three tubes fractured after a short time at high temperatures.

No definite conclusions regarding the feasibility of the process can be made from the information obtained. Further tests should be carried out on more suitable reactor tubes.

I. INTRODUCTION

The past decade has seen a tremendous increase in the production of synthetic organic chemicals using natural gas as the raw material. Natural gas, remarkably versatile in its applications, is available in large volumes at low cost. Each of the basic reactions, such as decomposition, oxidation, nitration, halogenation, pyrolysis and several others, gives rise to a family of primary organic chemicals which in turn are the building blocks for numerous other chemicals and products.

In Alberta, despite large and growing reserves of natural gas, the development of a chemical industry using natural gas has been very slow. A synthetic ammonia plant was built during World War II and a petrochemical plant is now under construction in Edmonton. One other plant, which will utilize hydrocarbon gases as the basic raw material, has been proposed. It is well known that the most serious deterrent to the establishment in Alberta of further natural gas utilization processes such as a carbon black industry, has been the comparatively small market within economic reach. This situation, however, is slowly changing and even today serious consideration is being given to the establishment of plants for the manufacture of a wide variety of products.

The Research Council of Alberta and the Department of Chemical Engineering of the University of Alberta have jointly inaugurated a long term research program on the industrial

utilization of natural gas. The principal objectives of this program are the technical investigation and commercial evaluation, under Alberta conditions, of certain hydrocarbon processes and the development within the Province of a center of knowledge concerning the current developments in this field.

The engineering and economic evaluation of the Pidgeon Process (26) for the manufacture of carbon black from natural gas undertaken in this investigation, is one phase of this program.

Carbon black, a generic term covering an important group of industrial carbons used chiefly as reinforcing agents in rubber and as coloring pigments in paints and inks, is produced from natural gas, oil enriched gas or oil. It has been used in the manufacture of inks and paints since the sixteenth century B.C. In 1910, an English rubber firm (33) investigating a large number of compounds as fillers for rubber, discovered the reinforcing properties of carbon black. At the present time 90% of all the carbon black produced is being used in the compounding of rubber. The United States, with its immense gas reserves, became the chief supplier of the world's carbon black requirements.

Carbon black is produced by three main processes involving the thermal decomposition of natural gas and the collection of the resulting carbon black. The processes vary in the way in which decomposition is accomplished. The physical and chemical properties of the carbon black depend largely upon the environment of the carbon particles immediately after the

decomposition of the hydrocarbon. The three processes are the Channel Process (19), the Furnace Combustion Process (11), and the Furnace Thermal Process (11).

The channel process, which accounts for about half of the total production, gives a high quality carbon black suitable for compounding in natural rubber. However, the yields are very low, 1.5 to 2.25 pounds of carbon black per thousand cubic feet of natural gas. The furnace combustion and thermal processes, although giving much higher yields, produce a carbon black of a different quality. The yields range from 4 to 16 pounds, depending on the grade being produced. As the quality of furnace and thermal black is made to approach that of channel black, the quantity recovered becomes only slightly more than the recovery in the channel process.

Much research work has been done and is being done on these processes to improve yield and quality of the carbon black produced. The channel process seems to have reached the zenith of its technical development, but the furnace combustion and thermal processes are relatively new - their products being best suited for compounding in synthetic rubbers.

A large number of patents for carbon processes have been issued. Most of these have to do with variations of the furnace combustion process. There are three other methods on which some development work has been done. One of these processes (25) involves the high temperature, normal pressure decomposition of natural gas in an electric arc with rapid quenching to prevent polymerization of the low molecular weight hydrocarbons formed.

The main products of this process are carbon black, acetylene, ethylene and hydrogen. This process is not suitable for Alberta because of the lack at present of cheap electric power. Another method (34) involves the explosion of a mixture of acetylene and natural gas or refinery gases with a limited amount of air. Due to the present high cost of acetylene, this method does not appear economically feasible. A third method, the Pidgeon Process (26) investigated on a laboratory scale, shows some promise. The process was suggested by Dr. L. M. Pidgeon for the National Research Council some fifteen years ago. In his preliminary investigation, Dr. Pidgeon claimed a recovery of 19 pounds of carbon black per thousand cubic feet of natural gas. The carbon content of one thousand cubic feet of gas is about 32 pounds. The carbon black was found to be similar to good grade thermal blacks.

There are several important factors to be considered in the proposal of a carbon black process suitable for development under Alberta conditions.

The carbon black industry is in a state of rapid technological development. The introduction of several new synthetic rubbers has necessitated the development of new grades of carbon black. New compounding techniques such as the introduction of carbon into rubber in the latex stage (called masterbatching), has led to the development of oil black, the best suited for this purpose. Oil black is made by modified furnace combustion black processes, such as the Phillips Petroleum Company's process,* using catalytic cycle stock or

---

* Pictured Flowsheet, Chemical Engineering, 58, No. 7, 176 (1951)

other cheap oils. The best location for a furnace oil black plant would be right next to a synthetic rubber plant, since the carbon black could be transported by pipeline in the form of a water slurry and incorporated directly into the latex. This would save a great deal on handling costs.

The Canadian consumption of carbon black amounts to about 50,000,000 pounds annually (6). Probably one half of this consists of three grades of channel black and the rest consists of about six different grades of furnace black. By present methods of production, a plant to supply Canadian needs, would involve a plurality of small units. It has been suggested (37) that a furnace black plant is economical to operate only if it produces over 12,000,000 pounds of carbon black per year. There is little possibility of entering the world market because of the high cost of transportation from Alberta to the seaboard.

The policy of the Alberta government which operates through the Petroleum and Natural Gas Conservation Board, would prohibit the installation in Alberta of any natural gas consuming industry which does not make reasonably effective use of the natural gas raw material. It is understood that the Conservation Board take the view that channel black plants with their low conversion efficiency do not represent efficient utilization of natural gas. The policy, however, is not one which automatically prohibits carbon black manufacture, but which will require carbon black production by an efficient process.

The laboratory scale investigation of the Pidgeon process indicates that good grades of carbon black can be

produced with a high recovery. Further investigation of the process may reveal that by varying the conditions of the decomposition reaction several grades of carbon black can be produced with the same equipment.

II. FUNDAMENTAL CHARACTERISTICS OF CARBON BLACK

Extensive electron microscope studies of carbon black (8) (9) have revealed the particles to be essentially spherical in shape. In carbon blacks made by certain methods, the particles appear to have varying tendencies to link up into chainlike structures (9). This effect is most pronounced in acetylene black and is least evident in the case of thermal blacks. High electrical conductance is associated with this structure.

X-ray diffraction work (7) has indicated the carbon black particles to be mainly crystalline in nature with some amorphous particles blended in. Particle size is in the range 5 to 35 millimicrons for channel black, 50 to 80 millimicrons for furnace black and 100 to 300 millimicrons for thermal black (9). The particles of a given sample of carbon black are not of a uniform diameter but show a distribution in size. Channel blacks are the most uniform and furnace thermal blacks show the greatest variation.

Carbon black consists chiefly of carbon with combined hydrogen and oxygen in varying amounts (14) depending on the method of manufacture. The hydrogen present in carbon black is residual hydrogen from the hydrocarbon raw material. It is presumably bonded to the carbon atoms in the quasi-graphitic lattice structure by true valence bonds. The oxygen present in carbon black is chemisorbed on the particle surface in the form of carbon oxygen complexes whose structure is still the subject of speculation. The amount of oxygen present appears to have

considerable effect on several secondary properties of the black.

Table I shows the composition of several types of carbon black.

TABLE I. COMPOSITION OF VARIOUS TYPES OF CARBON BLACK (10)

Blacks	C%[a]	O_2%[a]	H_2%[a]	Volatile Matter %	Ash%[b]	Moisture%[b]
High Color Channel (HCC-1)	88.4	11.2	0.4	17	0.10	6
Rubber Grade Channel (MPC)	95.2	3.6	0.6	5	0.10	4
Long Ink Channel (LIC)	90.0	8.7	0.8	12	0.10	6
Furnace Combustion (SRF)	99.2	0.4	0.3	1	1.00	1
Furnace Thermal	99.3	0.3	0.4	1	0.5	1

[a] Moisture-free basis

[b] Both moisture and ash values are a maximum rather than average

The scale of available types and grades of carbon black ranging from the finest channel black to the coarsest thermal black is termed the "Carbon Spectrum". The behavior of any of these carbons can be rationalized on the basis of three fundamental properties (31): 1. pH, 2. Surface, 3. Structure

pH: When a sample of carbon black is mixed into distilled water or a neutral salt solution, a definite, reproducible pH is established. The pH properties of carbon blacks were first described in 1937 (36). This investigation revealed that pH values ranged from 2.5 to 11.0 depending on the grade

of carbon black and its method of manufacture. Low or acid pH was shown to be intimately related to the volatile matter (C_x O_y complexes) on the carbon surface. No explanation has been offered to account for high or alkaline pH other than the absence of volatile matter.

This volatile matter was found to be responsible for the strongly selective adsorptive behavior of "acid" reinforcing carbons for alkaline substances and for alkaline rate of cure accelorators used in natural rubber compounding. pH is the preferred index to the rate of cure of carbon-rubber compounds.

Surface: For years the reinforcing action of carbon black in rubber was ascribed to the finess of the black used. The conjecture as to the size of carbon black particles was dispelled in 1940 (8) by the use of the electron microscope. The carbon black particles could now be seen and measured.

Based on these more precise size measurements, it was found that surface area across the carbon spectrum ranged from 1 to 32 acres per pound of carbon black. With this information the role played by particle surface in the reinforcement of rubber was rationalized. It was shown in 1942 (9) that carbon surface plays a dominant role in such reinforced rubber properties as plasticity, hardness, modulus, energy, tensile strength and rebound resilience.

Structure: Anomalies in the behavior of certain blacks having essentially the same pH value and surface area led to the introduction of the structure concept in 1942 (3, 9, 30, 35). The electron microscope revealed that the anomalous

behavior of these blacks was intimately associated with recognizable differences in their agglomeration and dispersion habits. The "low" anomalous carbons displayed a low degree of agglomeration in the dry state with a high degree of dispersability in the mixed condition. The "high" anomalous carbons on the other hand, showed a striking agglomeration habit in the dry state which took the form of a branched network rather than a clustered structure.

Dispersion tests revealed that the network type of agglomeration was very resistant to dispersion. In some cases the network structures were present after extensive milling. The property of carbons involving agglomeration habit with a corresponding wide variation in dispersion behavior was simply referred to as "structure". All carbons were described as having varying degrees of structure. Structure provides the index to anomalies in modulus, hardness, extrusion and related properties in rubber.

Closer study of the three fundamental characteristics of carbon blacks revealed further anomalies. The measurement of total particle surface by nitrogen adsorption isotherms (13, 27) and recognition of differences between electron microscope and nitrogen surface values, led to the introduction of "roughness factor" (2) as a possible new dimension of carbon black. This provided a quantitative measure of surface roughness or extension present, a property measurably affecting rate of cure when existent to any appreciable degree.

Evaluation of the probable behavior of colloidal

carbons in various rubbers by their fundamental characteristics seemed adequate until the development of fully reinforcing furnace combustion blacks and the introduction of "cold" rubber. "Cold rubber" is the term applied to a GR-S type of synthetic rubber produced by the polymerization of butadiene and styrene in a continuous process at a temperature of 41° F. Ordinary GR-S is primarily a copolymer of butadiene and styrene prepared at 122° F in a batch process.

Preliminary studies in "cold rubbers" consistently revealed significant differences between these carbons in the development of hardness properties that could not be adequately explained by their dimensional properties. Failure to resolve this modulus difference by exhaustive tests on the carbons, which revealed in the electron microscope as well as in other dimensional tests, substantial equality in fineness and structure, led to an investigation of various factors that contribute to the development of hardness properties in rubber compounds as a possible clue to this anomaly. In 1949, the Research Laboratories of Columbian Carbon Company (4 , 28, 32) showed that there was a new reinforcing element in cold rubber treads, viz. the carbon gel complex. This concept evolved out of "bound rubber" studies. Bound rubber refers to solvent insoluble rubber in association with carbon black. Carbon black gel complex or more simply carbon gel, refers to all the benzene insoluble rubber formed in unvulcanized carbon black rubber compounds. Although particle size, as well as structure influence carbon gel formation, a new property of carbon black was indicated,

viz., surface activity.

Through the evaluation of these basic carbon black properties by simple laboratory tests (11) and by recognition of the effects of these properties in the behavior of carbons in rubber, it is possible to predict fairly closely the behavior of any carbon of the spectrum in a rubber.

III. CARBON BLACK PROCESSES

Carbon black is the product of the thermal decomposition, at high temperatures, of gaseous or liquid hydrocarbons. Natural gas, from which most of the carbon black is produced, consists primarily of methane and ethane, the two most stable hydrocarbons.

The thermal decomposition of methane and ethane has been widely investigated but there has been little agreement as to reaction rates and the mechanism of decomposition. Egloff (12) lists 45 investigations of the thermal decomposition of methane and 21 for ethane. While free energy data indicate that methane is unstable above 575° C (16), it is generally agreed that the decomposition of methane proceeds at an appreciable rate only at temperatures above 800° C.

The decomposition of methane into its elements according to the equation

$$CH_4 \rightleftharpoons C + 2H_2 \qquad (1)$$

attains equilibrium only when a catalyst is present. Without a catalyst, equilibrium is not realized but the nature of the retarding force is not known. Table II shows the composition of equilibrium mixtures of methane and hydrogen at atmospheric pressure in contact with carbon as observed by Coward and Wilson (10).

TABLE II. EQUILIBRIUM MIXTURES OF CH_4 and H_2
THERMAL DECOMPOSTION OF METHANE

Temperature °C	CH_4 %	H_2 %
850	2.5	97.5
1,000	1.1	98.9
1,100	0.6	99.4

Investigations of the effects of catalysts on decomposition reaction have revealed two types of action; specific catalytic action and a surface action. Silica at times appears to retard and at other times to accelerate the decomposition reaction. The presence of a hot surface appears to facilitate the reaction but does not make it approach equilibrium more closely than a gas phase reaction. The carbon deposited on a surface is crystalline in nature and is of little commercial value.

Most carbonaceous materials, notably graphitic carbon, metals such as aluminum, cobalt, nickel and iron, and compounds such as calcium oxide, zinc oxide, nickel oxide, aluminum chloride and potassium hydroxide catalize the decomposition reaction. These catalysts lower the temperature of the reaction to the range 300° to 800° C. However, as in the presence of a hot non-catalytic surface, the carbon is deposited on the catalyst in a crystalline form.

The heat of reaction for the thermal decomposition of methane into carbon and hydrogen has been given by Parks

(20) as:

$$\Delta H = -15{,}450 - 11.1T + 0.0081T^2 - 0.0000012T^3$$

where ΔH = calories per gram mol

T = $^{\circ}K$

The reaction does not appear to proceed directly to the formation of carbon and hydrogen. Under certain conditions investigators have obtained traces of unsaturated hydrocarbons such as acetylene, ethylene, propylene, benzene, napthalene and tarry materials. This indicates the possibility of partial dehydrogenation with the formation of free radicals. The free radicals unite to produce the unsaturated hydrocarbons which then break down into carbon and hydrogen. Certain grades of carbon black produced at lower temperatures contain substantial amounts of tarry materials.

The decomposition of methane and ethane by partial combustion, as in the channel and furnace combustion processes, is not the result of preferential oxidation of the hydrogen of the hydrocarbons, but is due to the thermal cracking of the hydrocarbon in the oxygen free zone of the flames.

The fundamental characteristics of carbon black, surface area, pH, structure, roughness factor and surface activity for a given feedstock depend upon the following factors:

(1) Reaction temperature

(2) Time of contact

(3) Conditions after particle formation

These factors are described for the individual processes later in this section.

The surface area, a measure of particle size, depends upon the length of time the carbon black particles are exposed to high temperatures. Particle size is also somewhat affected by the molecular weight of the hydrocarbon. The pH of carbon black is associated with the $C_x O_y$ complexes formed on the surface of the carbon particle by the reaction of H_2O, CO_2 and O_2 with the carbon. At higher temperatures, reaction of the carbon particle surface with these oxidizing gases is rapid but the carbon complexes tend to be driven off almost as fast as formed, carrying away as mono- and dioxides. This results in an extension of specific surface presumably due to the etching of the carbon particle surface to produce irregularities. Surface extension is indicated by the value of the roughness factor. No explanations have been advanced for the conditions affecting structure formation and surface activity.

THE CHANNEL PROCESS

In the channel process the high temperature and heat requirements are obtained by the combustion of natural gas in a small uninsulated diffusion flame. The oxygen for combustion is supplied by diffusion through the invisible outer layer of carbon dioxide. The combustion in the outer layer supplies the heat required to thermally decompose the natural gas in the inner core of the flame into carbon and hydrogen. The sudden cooling to prevent agglomeration and combustion of the incandescent carbon particles is accomplished by impinging the flame on a relatively cool surface; 8 to 10 inch standard iron channels are used for this purpose. The temperatures range from

1,000° C to 1,200° C in various parts of the diffusion flame. The channels are maintained at a temperature of about 500° C. An almost unlimited volume of air is supplied but the conditions are adjusted to prevent complete combustion.

The period of time from the formation of the carbon particles to the sudden cooling by impingement is less than 0.1 seconds (29). Little time is available for particle growth after nucleuses formation, hence the small particle size of channel black. For several seconds after deposition on the channel, the carbon black is exposed, at 500° C, to an atmosphere containing CO_2, H_2O, O_2 resulting in the formation of C_x O_y complexes on the particle surface. Apparently oxygen is added until the surface is almost saturated. This treatment does not result in surface development to any great extent.

THE FURNACE COMBUSTION PROCESS

In this process natural gas is burned with insufficient air in a special furnace. The air and gas are injected into the fire chamber in alternate layers that are in laminar flow; combustion takes place in the diffusion layers at the interfaces. Only about 50% of the air theoretically required to burn all of the natural gas raw material to carbon dioxide and water is injected. All of this air is consumed rapidly by combustion to carbon mono- and dioxides and water in the first 10% to 20% of the furnace length. The flames may be described as nonpremixed flames burning in a mildly turbulent insulated enclosure. The unburned portion of the natural gas is almost

completely decomposed into carbon and hydrogen.

The black made in this process is exposed to temperatures of 1,100° to 1,400° C for 1 to 5 seconds (29). At this temperature level, reactions between the carbon black particles and CO_2 and H_2O occur at a rapid rate, resulting in an extension of specific surface. The $C_x O_y$ complexes formed on the particle surface are driven off because of the high temperature.

The relatively long contact time (i.e. retention time in the furnace at high temperature) results in a wide particle size distribution because nucleuses can continue to form during the period in which particles are growing in size. The hot carbon particles may act as a catalyst in the decomposition of more of the hydrocarbon gas.

The mean particle size, pH value, roughness factor, and structure are all affected by the retention time in the firechamber and the firechamber temperature.

The off-gas carrying the carbon black is quenched to about 210° C with water spray and the carbon black is collected in cyclones after agglomeration in an electric precipitator.

THE FURNACE THERMAL PROCESS

In the furnace thermal process the heat for decomposition is supplied by the preheated refractory materials with which the furnace is packed. The refractory material is preheated to 1,200° to 1,400° C. During the decomposition cycle the refractory is allowed to cool to about 900° C.

The retention time in the furnace is 3 to 4 seconds (34) and during this time about 98% of the hydrocarbon gas is

decomposed. More than half of the carbon formed is deposited on the refractory surface and the rest is carried in suspension by the off-gas. The carbon formed by decomposition on the refractory surface is crystalline in nature and even if it was recoverable, it would be of no commercial value. It is burned during the heating cycle to supply part of heat required for preheating the refractory packing of the furnace.

Part of the off-gas is sometimes recycled. It acts as a diluent for the decomposing natural gas. This dilution is so effective that it may reduce particle size to about one fifth of that produced by a straight run (18).

Particle size and other properties are affected by the retention time, the gas velocity past the refractory packing, the way the refractory packing is arranged and the degree of dilution. Since there is no H_2O, CO_2 or O_2 present during decomposition, pH and the roughness factor remain substantially constant for each particle size. Very little structure is apparent in carbon black produced by this process.

As the off-gas leaves the furnace, it is quenched to about 210° C with water spray. The carbon black is collected with a combination of electric precipitators and cyclones or by means of bag filters.

THE PROPOSED PIDGEON PROCESS

The essential feature of the Pidgeon process investigated on a laboratory scale, is the use of a refractory tube through the walls of which inert gases are diffused by means of a pressure differential to form a layer on the inside

wall of the tube. The purpose of this layer is to keep the decomposition reaction entirely in the gas phase. Deposition on the walls of the tube is undesirable because carbon black is a good insulator and the black formed on a hot surface is of no value.

The energy required for decomposition of the hydrocarbons is supplied by conduction and radiation through the walls of the tube. Flue gases from the furnace firechamber serve as the diffusing gas.

In this process time of contact and reactor tube temperature can be closely controlled. The presence of H_2O, CO_2 and O_2 in the diffusing flue gas makes the carbon black particles subject to after-treatment resulting in variation in pH and roughness factor.

The carbon black produced by this process with laboratory scale equipment had properties midway between those of channel and thermal black. The contact times used ranged from 0.1 to 1.2 seconds at temperatures of 1,360° to 1,390° C.

IV. THE PIDGEON PROCESS - A REVIEW OF PIDGEON'S WORK

In the carbon black production method (26) investigated on a laboratory scale by Dr. L. M. Pidgeon for the National Research Council in 1935, a "wall-free" reaction space was provided by diffusing inert gases through the wall of a permeable refractory tube. Dr. Pidgeon used a Norton Alundum tube, 15 inches long, 1 inch in diameter, with a wall thickness of 1/8 of an inch. The tube was heated in a gas fired furnace; the flue gas serving as the inert gas. The diffusion rate of the flue gas was controlled by varying the pressure across the wall of the tube. The furnace was operated at atmospheric pressure and a vacuum was maintained in the tube by means of a vacuum pump. The carbon black was collected on a cloth filter after the cooling of the cracked gas by means of water cooled baffles.

The tube was protected from direct flames by a periclase plate placed between the burners and the tube. The outside temperature of the tube was measured with a "Pythagoros" tube shielded platinum, platinum-rhodium thermocouple for the lower range of temperatures and an optical pyrometer for the higher temperatures. No attempt was made to measure the temperature of the gas during thermal decomposition.

Before each run the tube was calibrated for variation of rate of diffusion with differential pressure. The minimum rate of diffusion required to keep the carbon black from coating out on the walls of the tube was determined experimentally for

for each gas rate.

The experiments were conducted using a natural gas of the following composition: CH_4 85.1%; C_2H_6 13.5% ; N_2 1.4%. The tube temperature and time of contact were varied. The results of a number of experiments are reproduced in Tables III and IV.

TABLE III. PRODUCTION OF CARBON BLACK FROM METHANE-ETHANE

Experiment	1	2	3	4	5	6
Pressure, in. of water	6.8	2.4-3.1	1.4	0.2	7.5	1.4
Inlet rate, cu. ft. per min.	0.14	0.08	0.05	0.01	0.06	0.06
Diffusion rate, cu. ft. per min.	0.23	0.18	0.07	0.02	0.23	0.12
Outlet, cu. ft. per min.	0.40	0.21	0.12	0.04	0.28	0.15
Expansion %	21	0	0	-100	-16	-50
Temperature °C	1360	1380	1380	1380	1390	1390
Yield						
lb. per 1000 cu. ft.	12.8	18.3	17.7	10.7	16.8	16.9
% theory	37	53	51	31	49	55
Apparent time of contact, sec.	0.13	0.25	0.42	1.2	0.18	0.28
Inlet / Diffusion	0.6	0.6	0.6	0.6	0.26	0.26

TABLE IV. COMPOSITION OF OFF-GAS FROM PYROLYSIS OF METHANE-ETHANE AT 1,380°C

	Flue Gas	Experiment 1	Experiment 2
Apparent time of contact, sec.	--	0.13	0.25
Expansion %	--	21	0
Inlet / Diffusion	--	0.6	0.6
CO_2	8.8	3.8	2.0
CO	--	3.8	8.1
O_2	5.1	2.0	2.8
C_2H_2	--	2.1	1.9
Olefines	--	0.4	0.2
H_2	--	23.6	24.4
CH_4	--	8.8	2.6
N_2	86.1	55.5	58.0

The yields listed in Table III are based on the volume of inlet gas. Yields are usually stated for the total volume of gas which includes both the reaction gas and the gas required for heating.

The composition of the off-gas depends upon a number of factors; the degree of decomposition of the inlet gas, the diffusion to inlet gas ratio, the composition of the flue gas, the composition of the inlet gas and reactions taking place between the flue gas and the gas in the reactor tube. Several reactions are possible and the relative rates at which these reactions take place have a bearing on the composition of the off-gas.

The following reactions may take place:

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

$$C + CO_2 \longrightarrow 2CO$$

$$C + H_2O \longrightarrow CO + H_2$$

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

$$CH_4 + O_2 \longrightarrow CO + H_2 + H_2O$$

$$2C + O_2 \longrightarrow 2CO$$

Calculations of the heat available from the off-gas show that with proper design and facilities for heat exchange it may be possible to supply the heat requirements with the off-gas. For example: on off-gas of the composition shown in column 1, Table IV, has a heating value of about 190 Btu per cubic foot. To produce this off-gas, 37% of the inlet gas was decomposed and the ratio of inlet gas to diffusion gas was 0.6. The heat requirement for 37% thermal decomposition of one cubic foot of the gas is about 21 Btu at 1,400° C. The theoretical flame temperature for the off-gas is about 1,680° C and the heat available at 1,400° C is 58 Btu for each cubic foot of inlet gas. In actual practice, the theoretical flame temperature would not be attained and the available heat would be cut down by heat losses. (See Appendix D)

Figure I, a plot of Pidgeon's data, indicates an optimum time of contact for greatest yield. The inlet gas rate to diffusion gas rate ratio appears to have little effect over a limited range on the yield at the same contact time. This optimum time of contact is probably an individual characteristic of each tube size. Sufficient data were not available to show the effect of time of contact on the heating value of the off-gas.

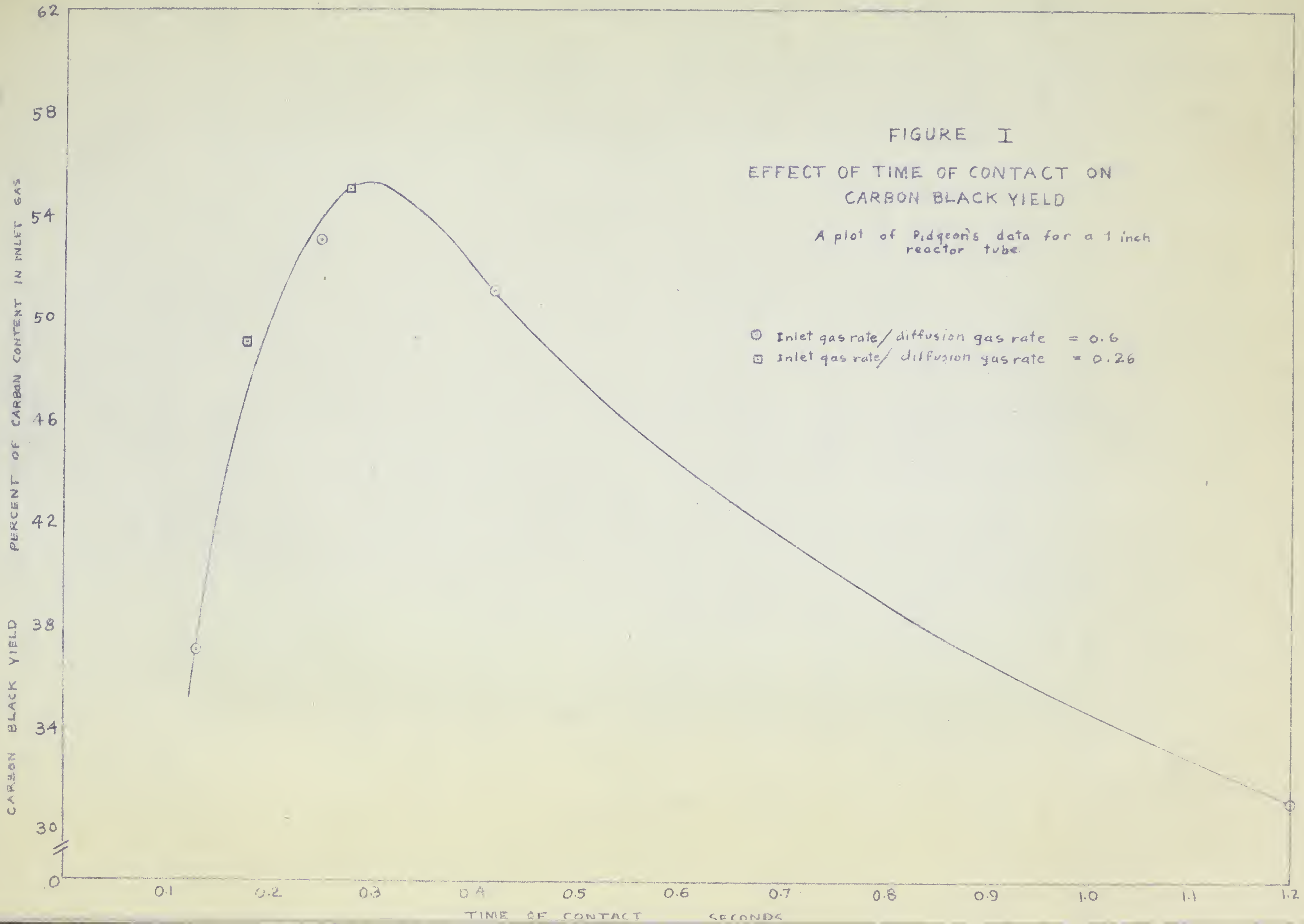


FIGURE I

EFFECT OF TIME OF CONTACT ON CARBON BLACK YIELD

A plot of Pidgeon's data for a 1 inch reactor tube.

The carbon black produced in Dr. Pidgeon's investigation showed rubber reinforcing properties very similar to those of furnace thermal black. A full investigation of the effects on yield and properties of different times of contact, dilution of the inlet gas and reaction temperature was not made.

There are so many factors affecting this process that data acquired on small scale apparatus cannot be extrapolated for use in the design of commercial equipment. The results of Dr. Pidgeon's investigation show that the process has possibilities and merits investigation on a larger scale.

V. EQUIPMENT DESIGN

The evolution and development of a process may be divided into five distinct stages:

(1) Laboratory stage

(2) Small sized model

(3) Large sized unit

(4) Semicommercial plant

(5) Commercial plant

The correctness of the technical principle of the process and the commercial soundness are tested in the first stage. Assuming that the laboratory stage yields favorable results, development passes to the small sized model. The purpose of this stage is to determine the optimum operating conditions, to evaluate the properties of the products and to obtain design data for a full sized unit. A preliminary investigation of the economics of the process is also made at this stage.

This investigation of the Pidgeon process represents a stage intermediate between the small sized model and the large sized unit. The equipment was designed to allow use of commercial size reactor tubes and standard materials in its construction.

The essential requirements of the equipment may be stated as follows:

(1) a means of heating the reactor tube and providing inert gases for diffusion into the tube

(2) a method of applying a pressure differential across the walls of the tube to provide the driving force for gas diffusion

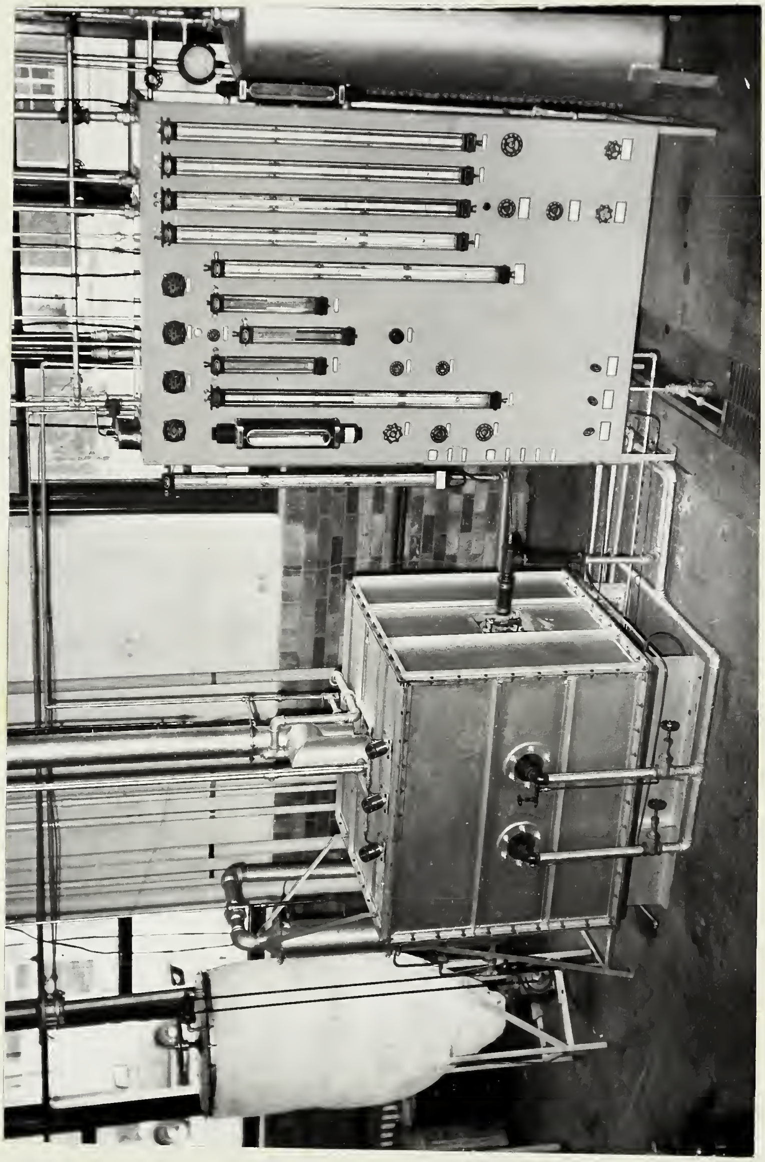


Fig. II. View of complete unit

(3) provision for reactor tube temperature measurement

(4) a means of supplying and metering natural gas to the reactor tube

(5) a method of quenching the off-gas to prevent agglomeration of the carbon black

(6) provisions for the collection of the carbon black

(7) provisions for the measuring and controlling of flowrates, temperatures and pressures

The first step in the design was the choice of a reactor tube diameter. Commercial tubes were available in diameters of 1, 2 and 3 inches. The equipment was designed for a 3 inch diameter tube, but provisions were made for the testing of 1 and 2 inch diameter tubes. The tubes were obtained from the Norton Company of Worcester, Mass. This firm also supplied the tubes for Dr. Pidgeon's investigation.

The Norton Alundum RA 1139 permeable aluminum oxide tubes were 3 feet long and had an inside diameter of 3 inches and a wall thickness of 1/4 of an inch. The diffusion rate through walls of the cold tubes was of the order of 0.5 cubic feet per minute per square foot under a pressure differential of 2 inches of water.

It was decided that a furnace in which the reactor tube is horizontal would be the easiest to build. A minimum fire chamber length of 2 feet necessitated the extension of the 3 foot reactor tube. This was accomplished by cementing into one end of the reactor tube a Norton Alundum RA 1139 tube

18 inches long with an inside diameter of 2 inches and a wall thickness of 3/8 of an inch. To maintain a pressure differential of several inches of water between the reactor tube and the furnace firechamber, two methods were available; pressurization of the furnace or application of a vacuum to the reactor tube. Both of these methods were incorporated into the design.

Pressurization of the furnace necessitated the construction of airtight steel shell over the brickwork of the furnace (See Figures III and IV). The case consisted of 16 gauge black iron sheets spot welded to 1 inch angle iron frames. The panels were bolted together with 1/4 inch machine bolts. Rubber gaskets were used at all joints. The base of the furnace consisted of a 1/4 inch steel plate mounted on a channel and I-beam framework.

Preliminary operation showed that it was necessary to pressurize the space between the case and brickwork to prevent overheating of the case by hot flue gas leakage from the firechamber.

To make the reactor tube and furnace firechamber pressure control more versatile, jet ejectors were installed on the flue gas and off-gas discharge lines (See Figure V). These ejectors consisted of a 2 inch 90° elbow and a venturi section with a throat diameter of 1 inch and wall to axis angles of 7° and 15°. A section of 1/4 inch standard iron pipe reaching within 1/2 inch of the throat was used as the nozzle. These jet ejectors were found to have a large capacity and at no load developed 24 inches of water vacuum with a line air pressure of

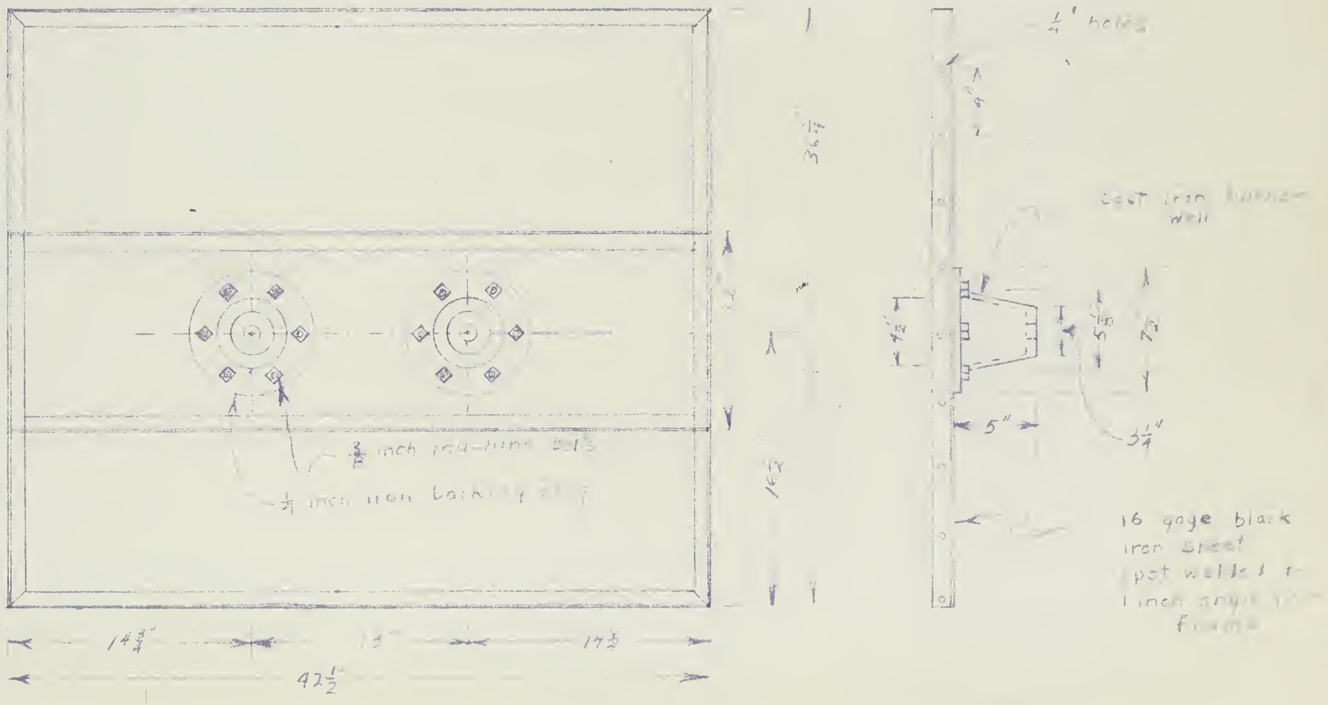


FIGURE III A

FURNACE JACKET SIDE PANEL

SCALE 1" = 12"

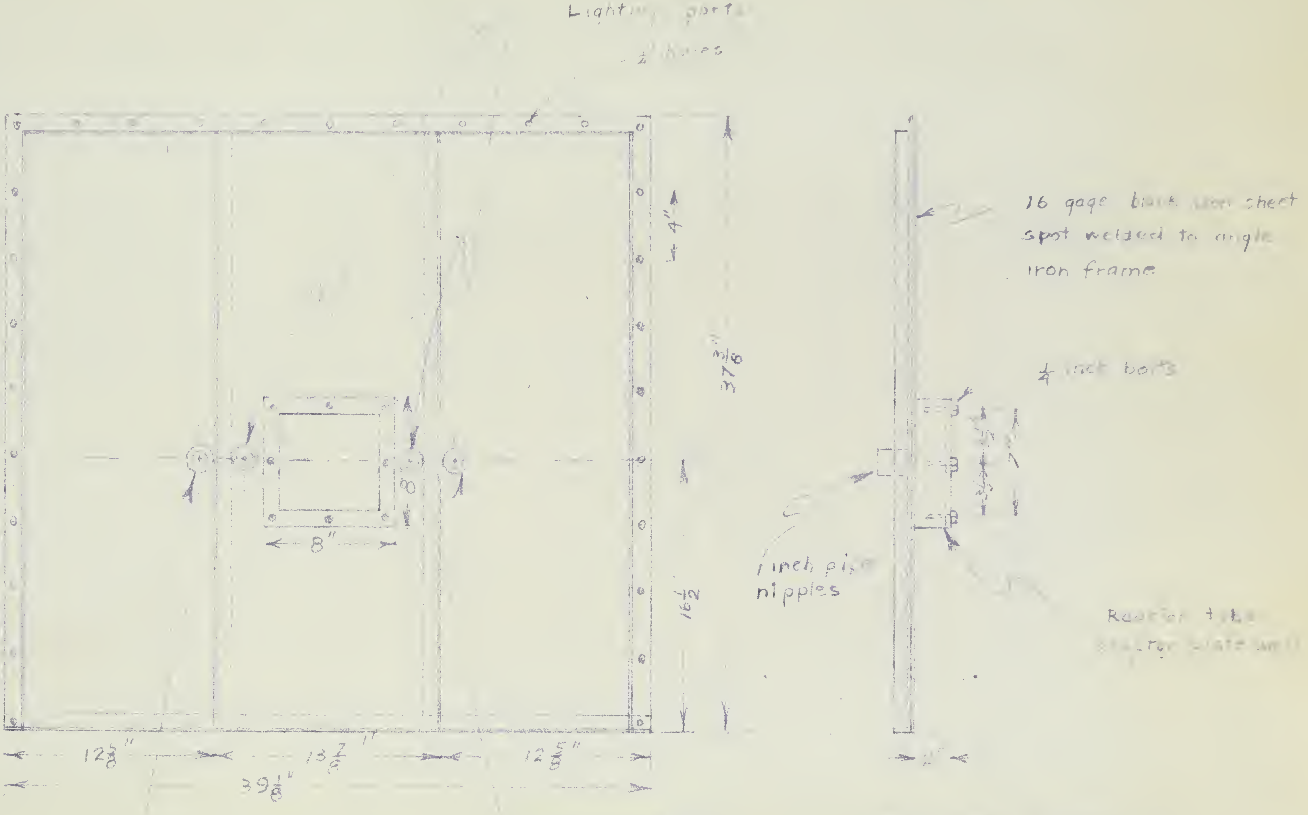


FIGURE III B

FURNACE JACKET END PANEL

Scale 1" = 16"

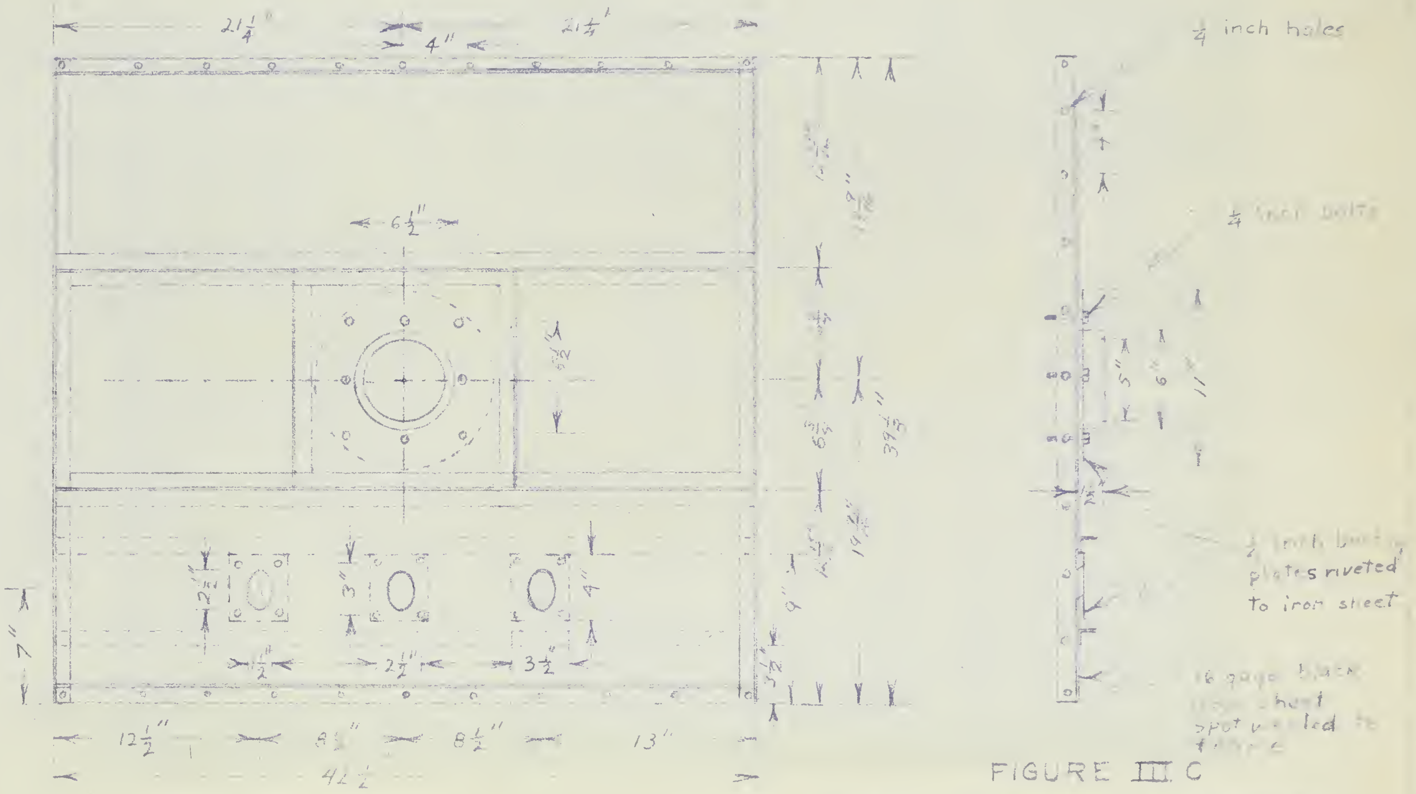


FIGURE III C

FURNACE JACKET TOP PANEL

scale 1" = 10"

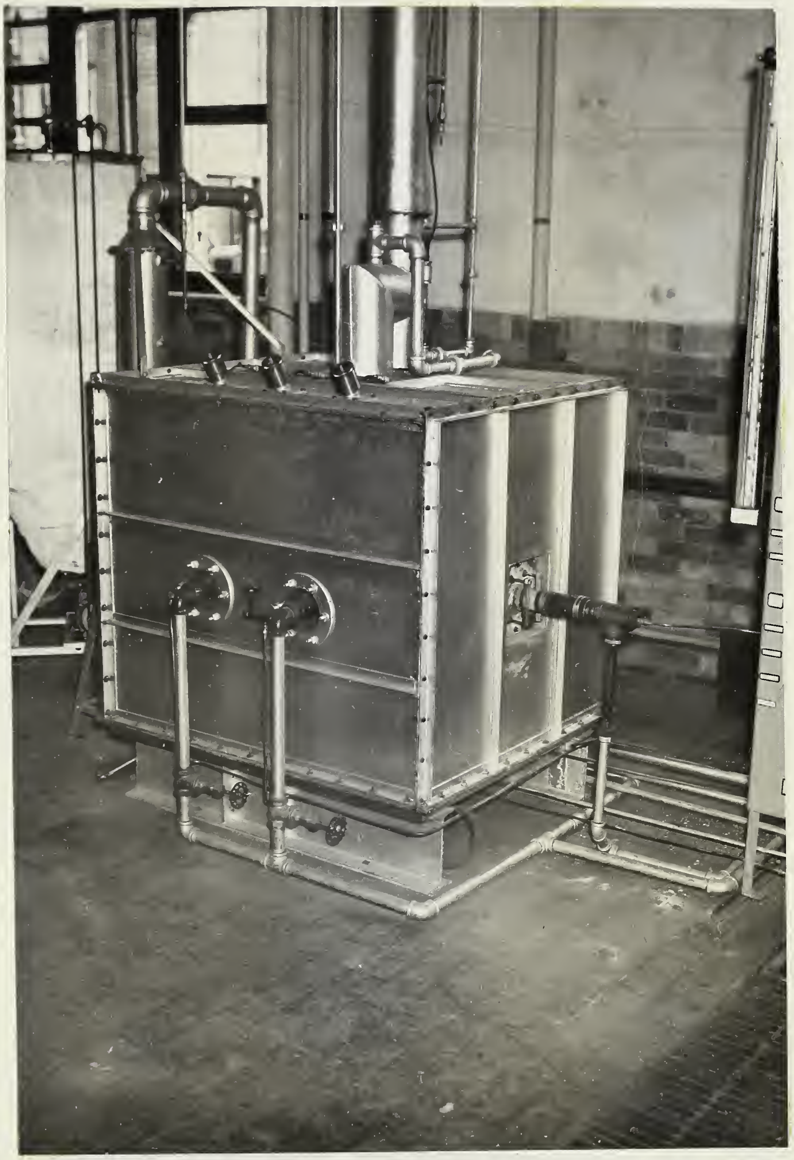


Fig. IV. The furnace

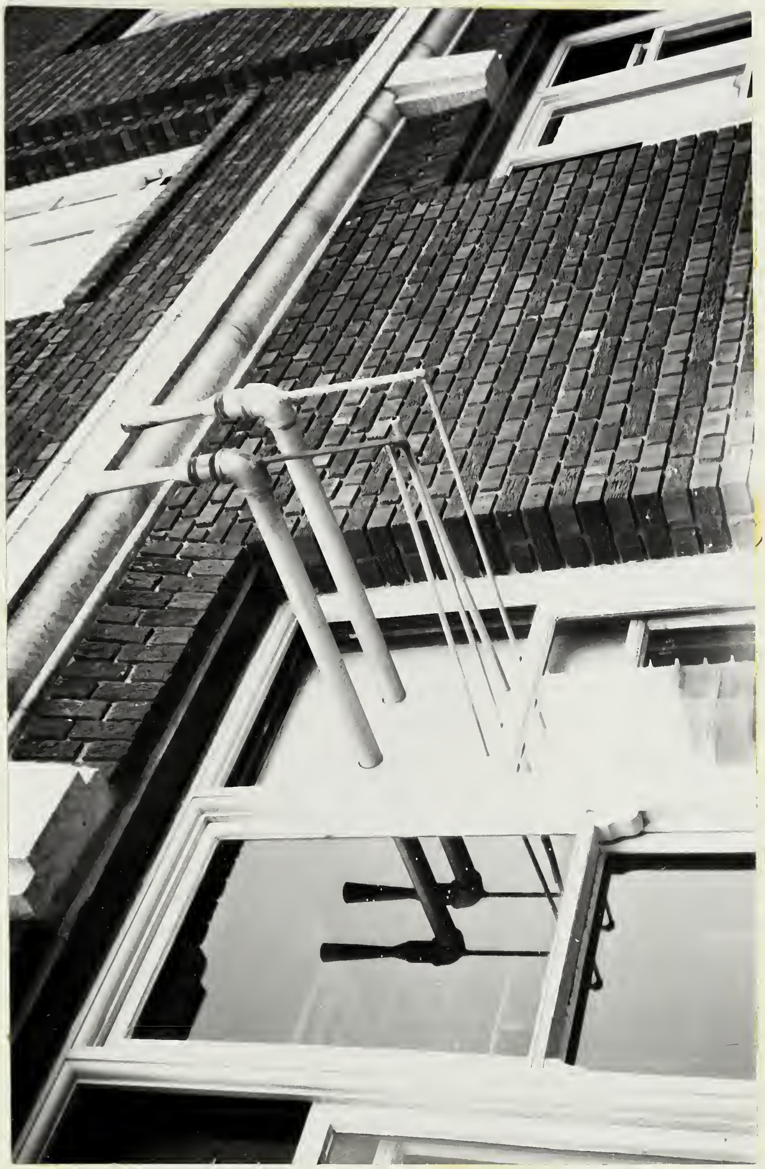


Fig. V. A view of the jet ejectors

40 psi. It was found that the furnace operated more evenly if the firechamber was maintained at atmospheric pressure. The pressure differential across the walls of the tube was obtained by putting a vacuum on the reactor tube by means of the jet ejector.

Fire brick able to operate continuously at temperatures of 1,600° C was necessary for the firechamber. For insulation a 4½ inch layer of insulating firebrick and a 3 inch layer of A.P. Green block insulation were used. A.P. Green Fire Brick Co. Ltd. products; Mex-ko fire brick, G-23 insulating fire brick and Sairset high temperature mortar were used in the construction. Special shapes were made from plastic firebrick. The brickwork is shown in Figures VIII to X.

To prevent flames from impinging directly on the tube and to provide for a more even temperature distribution along the reactor tube, silicon carbide plates 8 x 24 x 1 inches were installed between the burners and the tube.(See Figure X).

Dr. Pidgeon's investigation showed that 0.1 seconds was about the minimum time of contact for the flame temperatures obtainable with an air-natural gas fuel mixture which was not preheated.

The heat requirements for the 3 inch reactor tube were calculated on the basis of 60% decomposition of natural gas, a contact time of 0.1 second and the flue gas diffusion rate used in most of Dr. Pidgeon's runs (See Appendix A-1). The heat output required to supply 12,000 Btu per hour at 1,400° C for decomposition and to allow for heat losses was

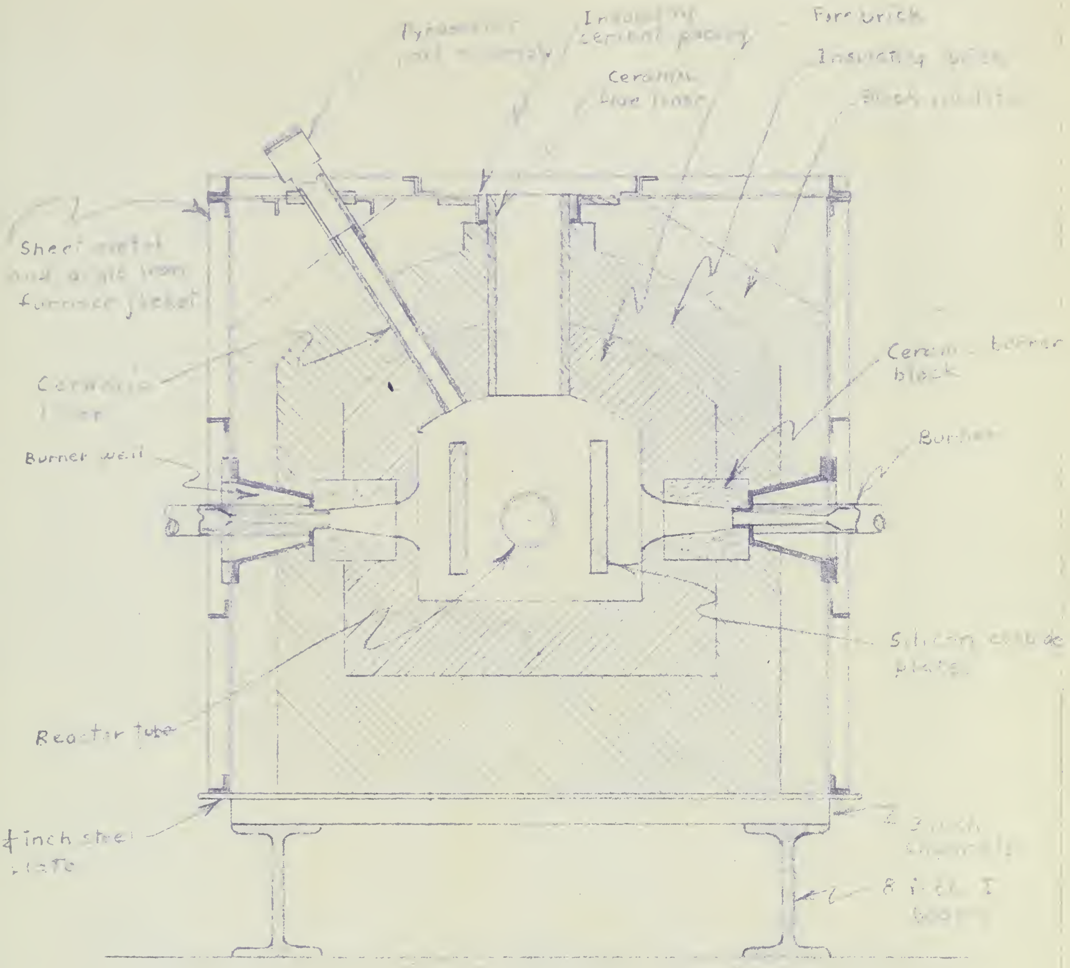


FIGURE VI

TRANSVERSE CROSS-SECTION OF FURNACE

Scale - $\frac{1}{10}$ full size

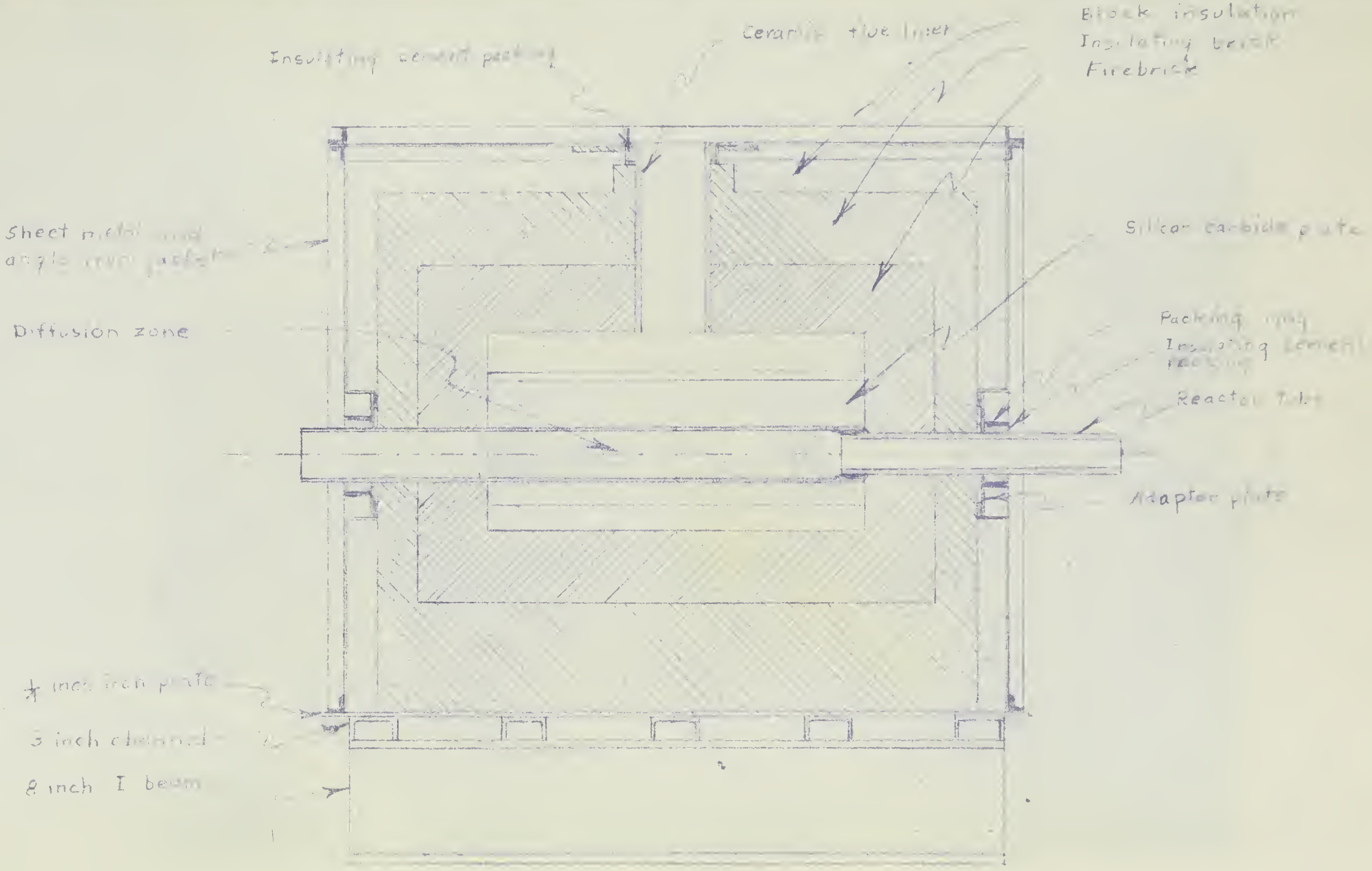


FIGURE VII

LONGITUDINAL CROSS-SECTION OF FURNACE

Scale - $\frac{1}{12}$ full size

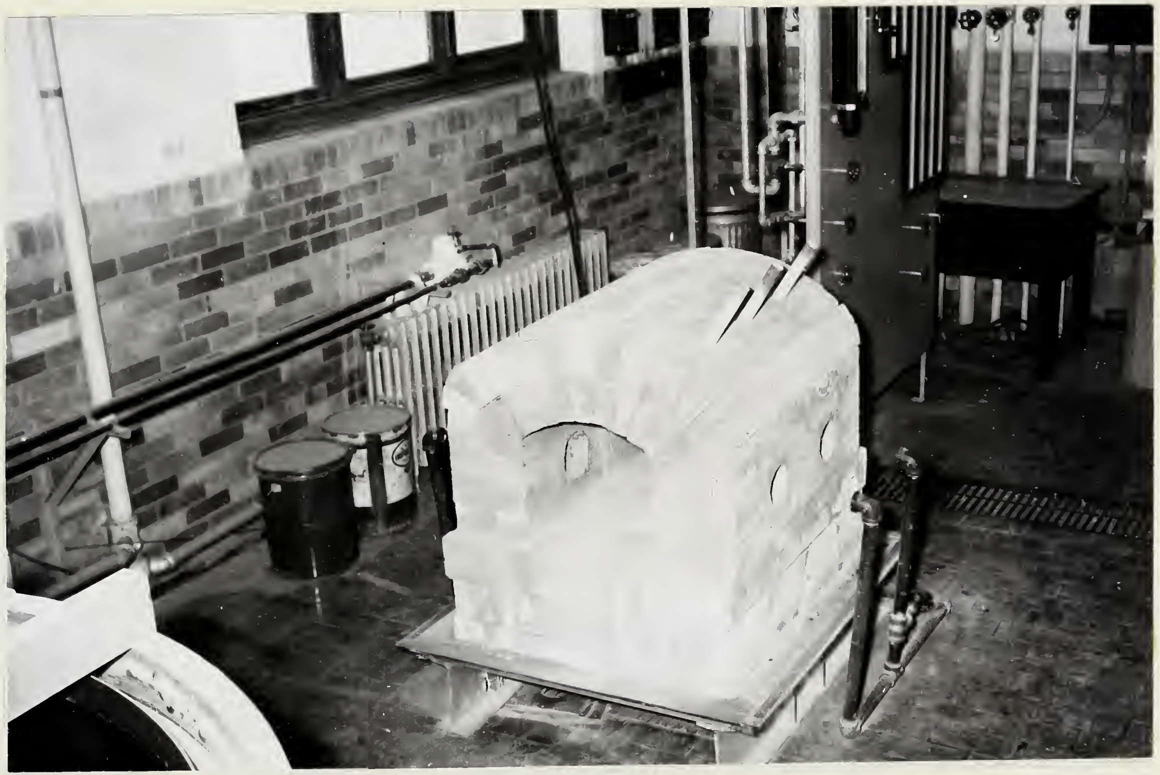


Fig. VIII. A view of the incomplete brickwork

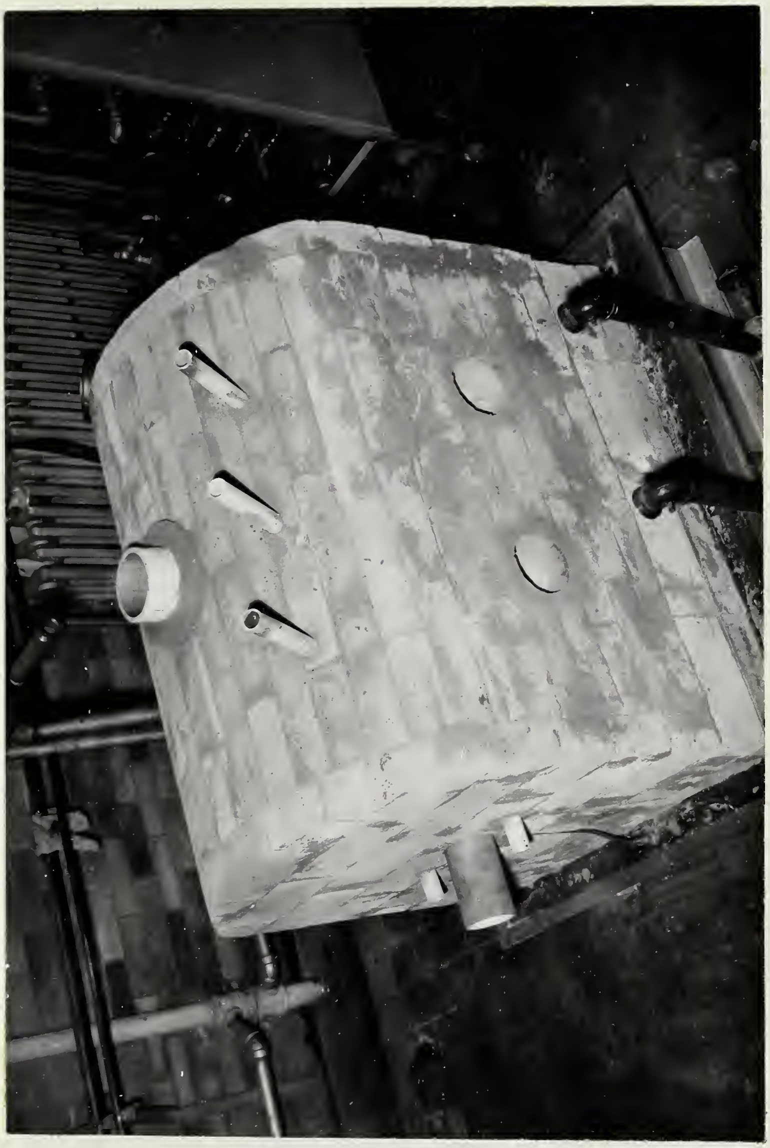


Fig. IX. The complete brickwork of the furnace

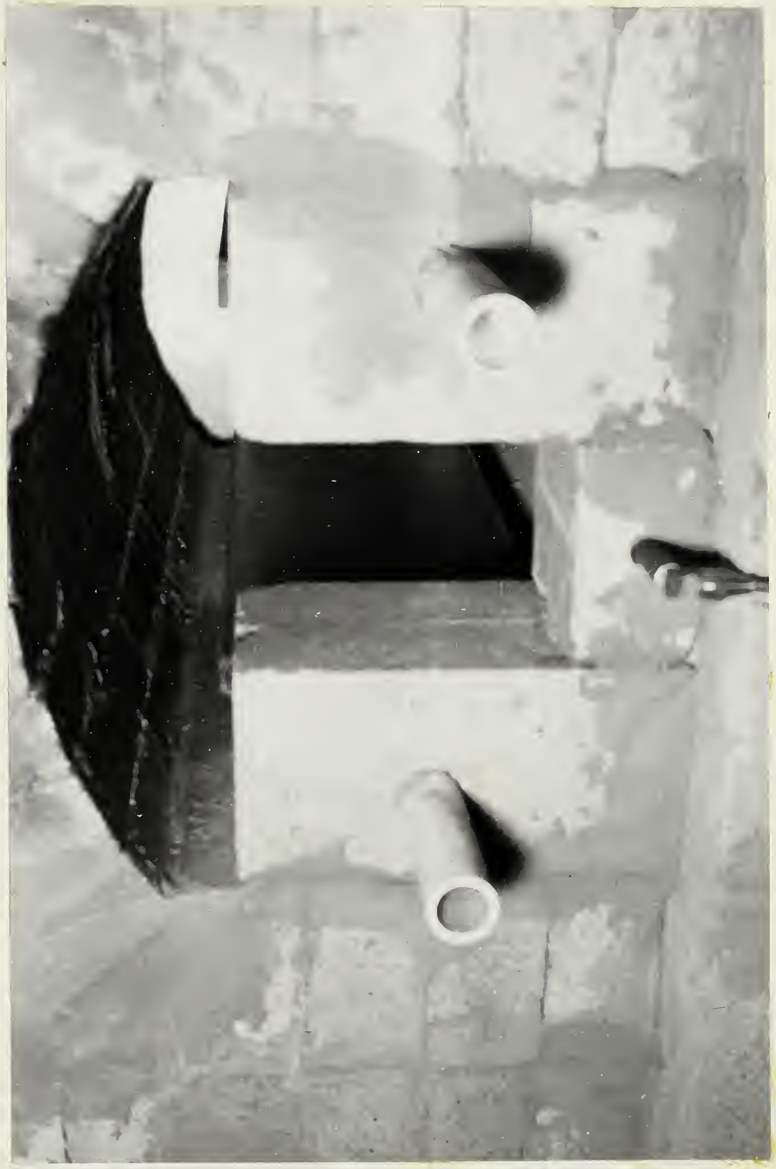


Fig. X. Lighting ports and silicon carbide plate mounting

calculated to be 100,000 Btu per hour. Four Eclipse Fuel Engineering Company #2HBA burners and a #44-14LP proportional mixer with a 1 inch zero gas governor were used to supply the heat load. Air and natural gas for the proportional mixer were obtained from existing laboratory service mains.

No arrangement for venting high temperature gases existed in the laboratory making it necessary to cool the flue gases before venting to the outside through uninsulated iron pipe. Cooling of the flue gases to 200° C was accomplished by water spray in a cooling tower of 5 inch steel tubing $5\frac{1}{2}$ feet long (See Figure XI). Three Spraying Systems Co. #1/8 GG1 nozzles were used to handle the 21.5 gallons of water required for cooling. To make certain that no water was sprayed into the furnace through the 4 inch diameter ceramic flue lining (Norton Alundum) the spray tower was offset. The water cooled jacketed offset elbow was made of stainless steel because of the possibility of corrosion. The nozzles were connected to a line filter in the water supply line by means of copper tubing. Water at 20 psi from the laboratory service main was used to supply the spray system. A warning system consisting of contact points in the quench unit drainage sump, a relay, a panel light and a bell was incorporated into the unit to warn of flooding (See Figure XII).

The furnace was lit by means of a spark gap on a wand inserted into the furnace through lighting ports. The ports were lined with 1 inch inside diameter aluminum oxide tubes (See Figure X). High voltage current for the spark gap was

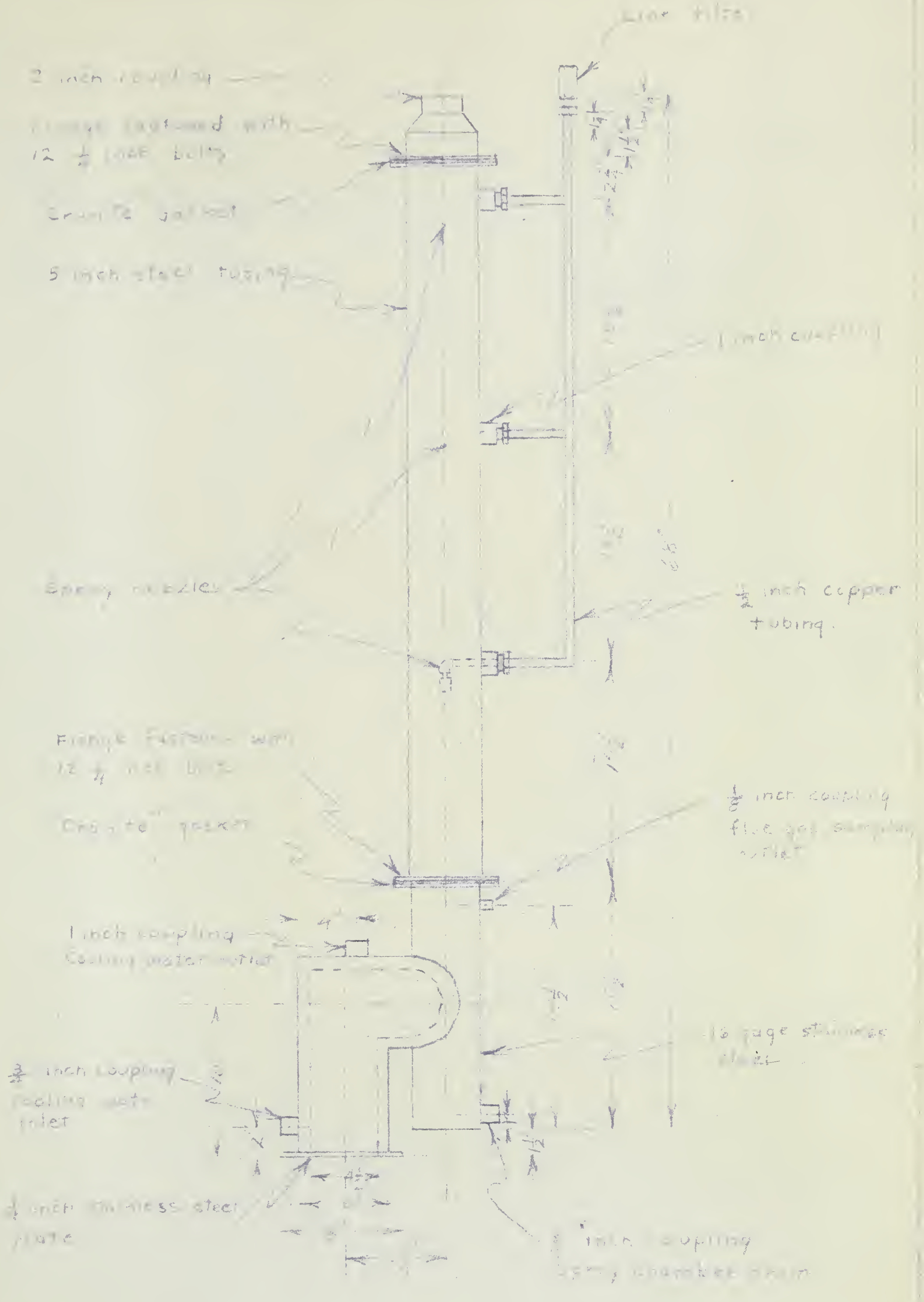

Line filter
2 inch coupling
Flange fastened with 12 ¼ inch bolts
Durite gasket
5 inch steel tubing
1 inch coupling
Spray nozzles
½ inch copper tubing
Flange fastened with 12 ¼ inch bolts
Durite gasket
⅛ inch coupling flue gas sampling outlet
1 inch coupling Cooling water outlet
4"
⅜ inch coupling cooling water inlet
16 gage stainless steel
¼ inch stainless steel plate
4½"
6"
8"
½ inch coupling spray chamber drain

FIGURE XI FLUE GAS QUENCH UNIT [illegible]

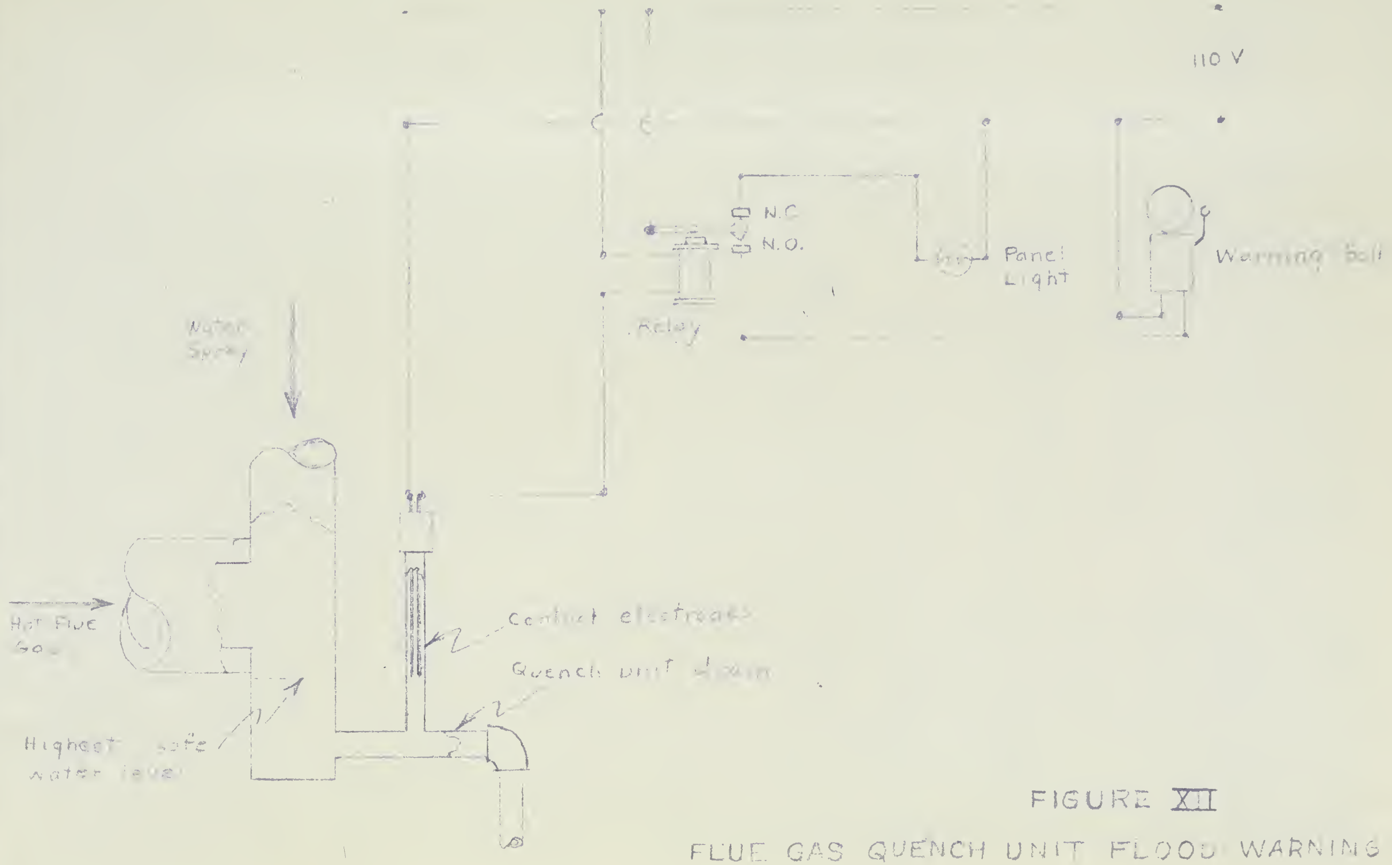


FIGURE XII

FLUE GAS QUENCH UNIT FLOOD WARNING SYSTEM

supplied by an induction coil drawing current from a six-volt storage battery. Valves on the manifold leading to the burners permitted lighting of each burner individually.

The diffusion rate of the flue gas into the reactor tube was controlled by varying the pressure in the firechamber and tube. The pressures were varied by means of the jet ejectors on the flue gas and off-gas exhaust lines and by a butterfly valve on the flue gas exhaust line.

The natural gas supply for the reactor tube was obtained from the laboratory service main. Since the main pressure was only 9 inches of water, it was necessary to compress the gas. A 3 inch bore, 3½ inch stroke Curtis compressor driven by a 1 horsepower electric motor was used. The gas was passed from the compressor through an oil removal filter to a 6 cubic foot surge tank (See Figure XIII). The oil removal filter was packed with 1 foot of 1/4 inch raschig rings, 6 inches of glass wool and 6 inches of granulated charcoal. From the surge tank, the gas was passed through a pressure reducer and into a rotameter for flow rate measurement. The compressor was switched on and off by a pressure switch actuated by surge tank pressure. Air and nitrogen lines were installed to purge the reactor tube. The compressor crankcase was vented to the outside through 1/4 inch pipe.

The surface temperature of the reactor tube was measured with a Leeds Northrup #8621 optical pyrometer through quartz window pyrometer ports. Quartz windows were used because of their low radiation absorptivity. Temperature measurements

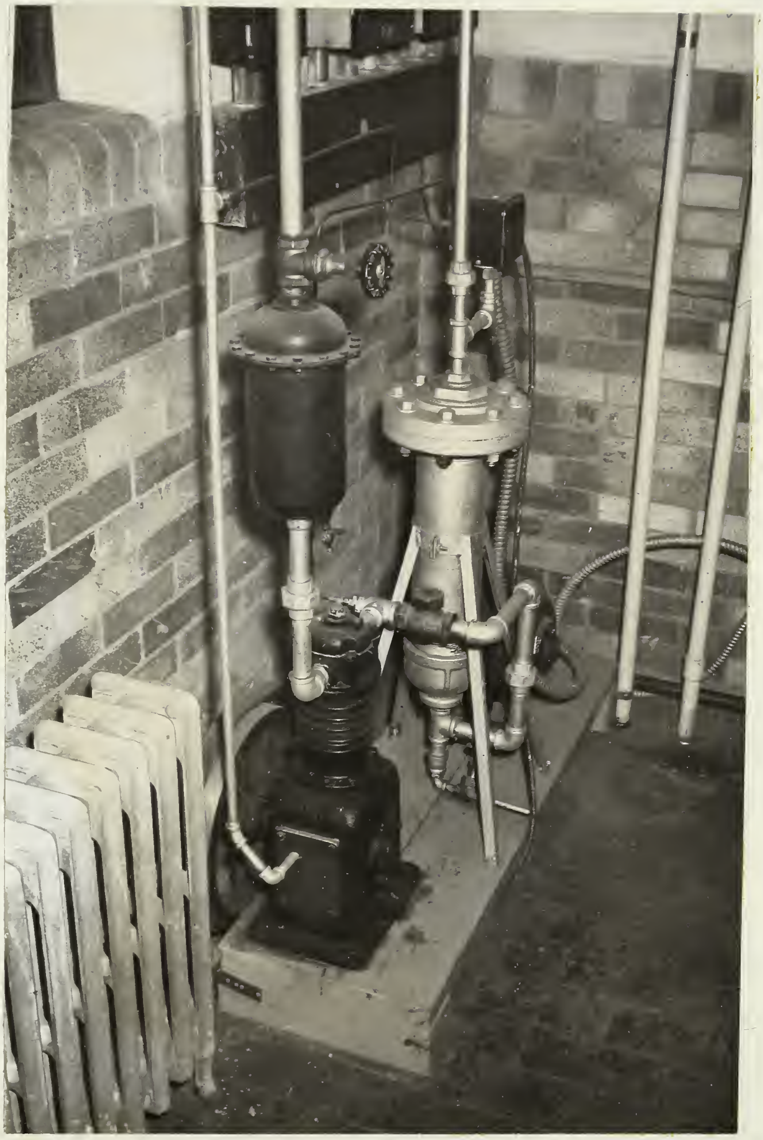


Fig. XIII. Compressor installation

were made on the section of reactor tube in the fire chamber at 3, 11½ and 20 inches measured from the outlet end. Three aluminum oxide tubes of 1 inch inside diameter, running through the steel case insulation and brickwork served as the sighting tunnels. The opening at the top of each tube was sealed off by means of a special flange mounted quartz window holder (See Figures IV and XIV). To cool the pyrometer ports and to help keep the inside of the quartz windows from being coated with dust, compressed air was blown into each port just below the quartz window.

To quench the off-gas immediately after its exit from the reactor tube, a water spray tower type of quench unit was used (See Figures XV and XVI). This unit was made from 16 gauge stainless steel sheet. Stainless steel was necessary to prevent corrosion and contamination of the carbon black with iron oxide. The cooling was accomplished in a spray chamber 6 inches in diameter, 3 feet high, equipped with 2 Spray Systems #1/8 GG1 nozzles. A flood warning system similar to that in the flue gas quench unit was installed. The design calculations are shown in Appendix A-3.

Originally a collection system involving the agglomeration of the carbon black with high frequency sound and its collection with a cyclone was considered, however, the high cost of a suitable sound generator necessitated the abandonment of this scheme in favor of a bag filter unit.

The bag filter unit consisted of a cylindrical sheet metal housing containing three glass cloth bags 6 inches in

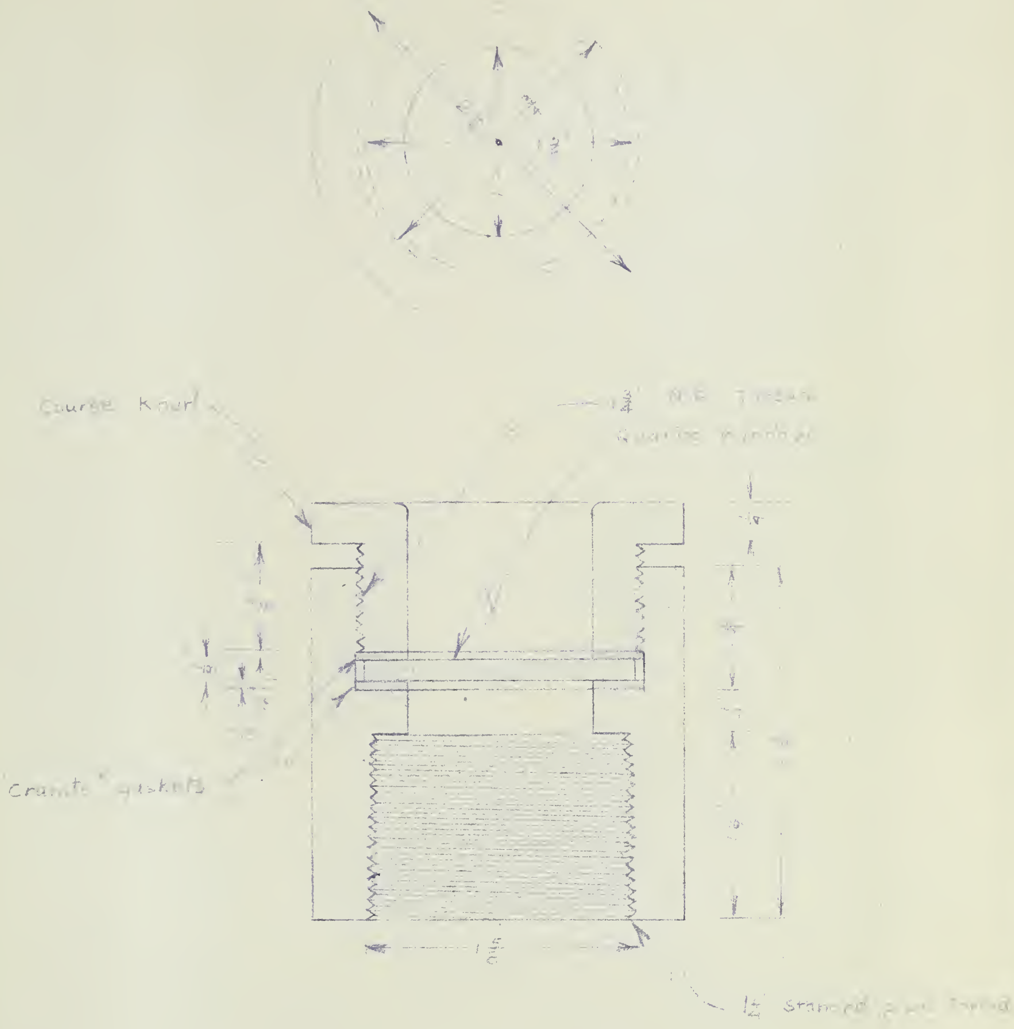


FIGURE XIV

PYROMETER PORT QUARTZ WINDOW MOUNTING

Scale full size

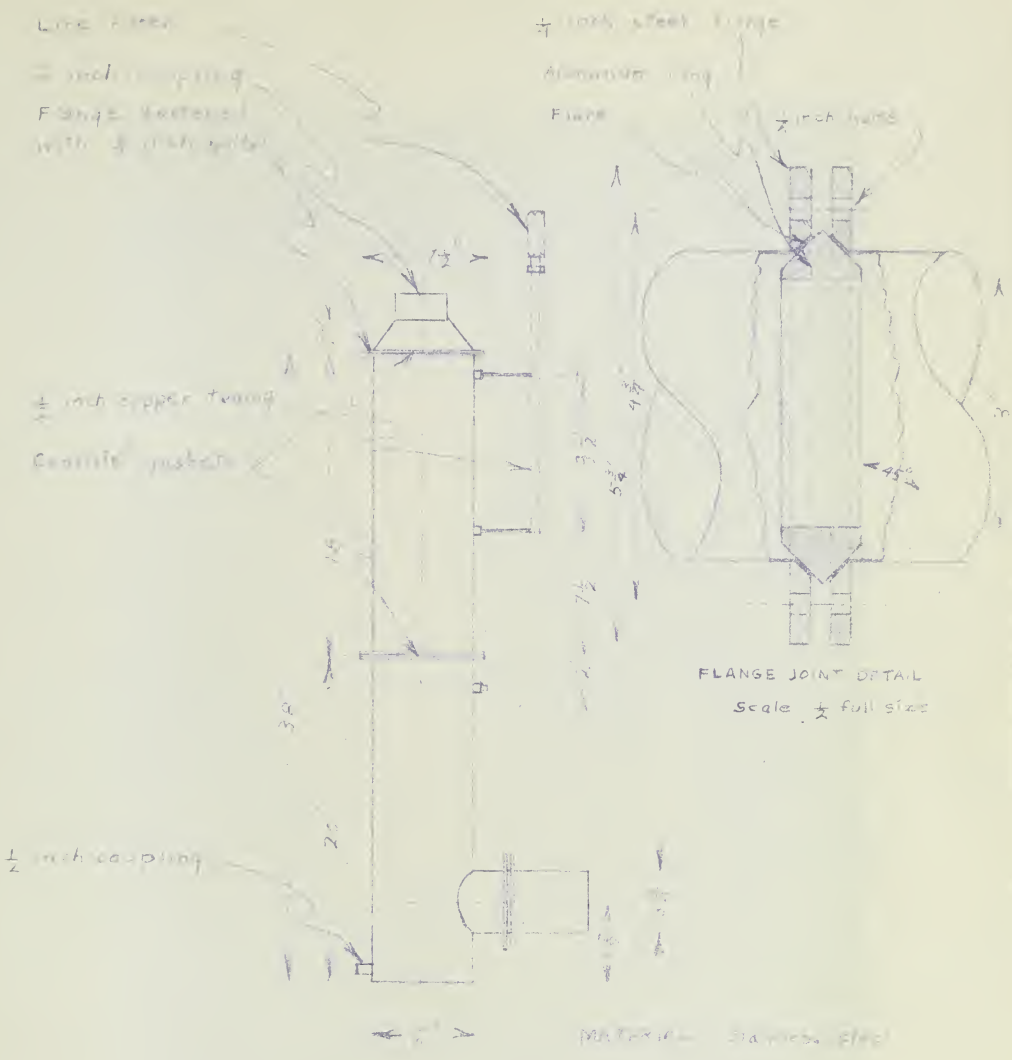


FIGURE XV

OFF - GAS QUENCH UNIT

Scale 1/10 full size

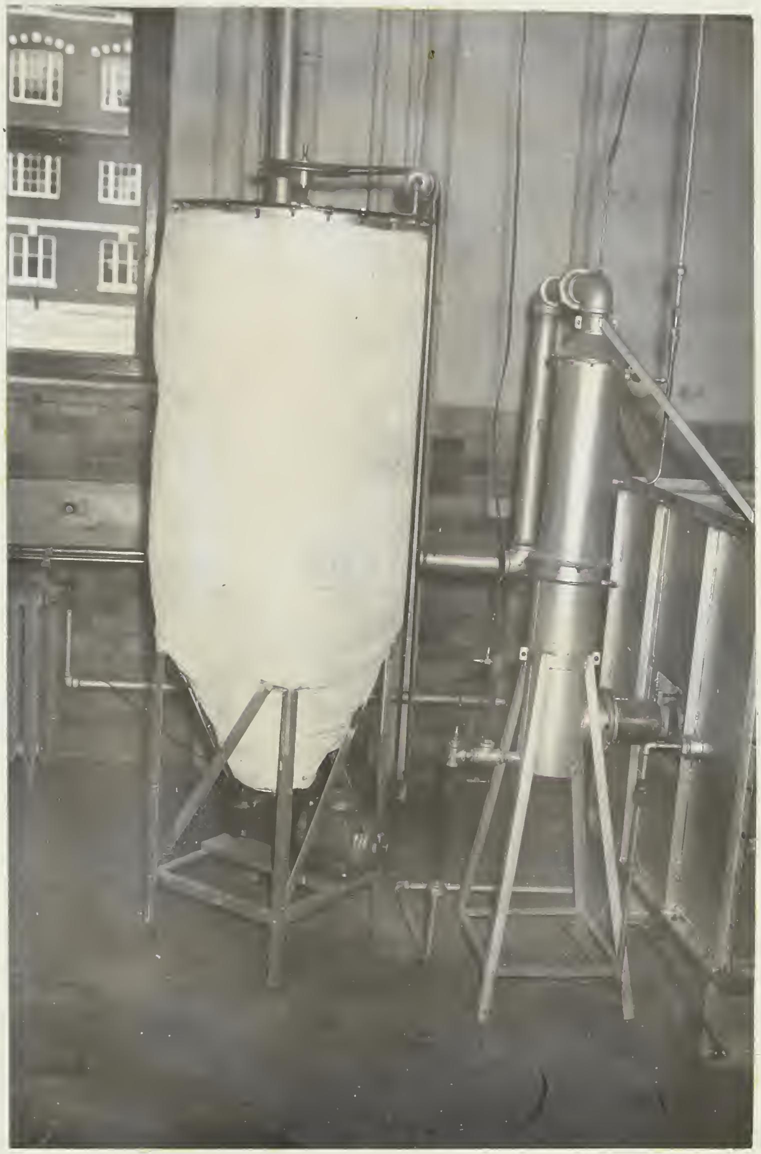


Fig. XVI. Bag filter unit and off-gas quench unit

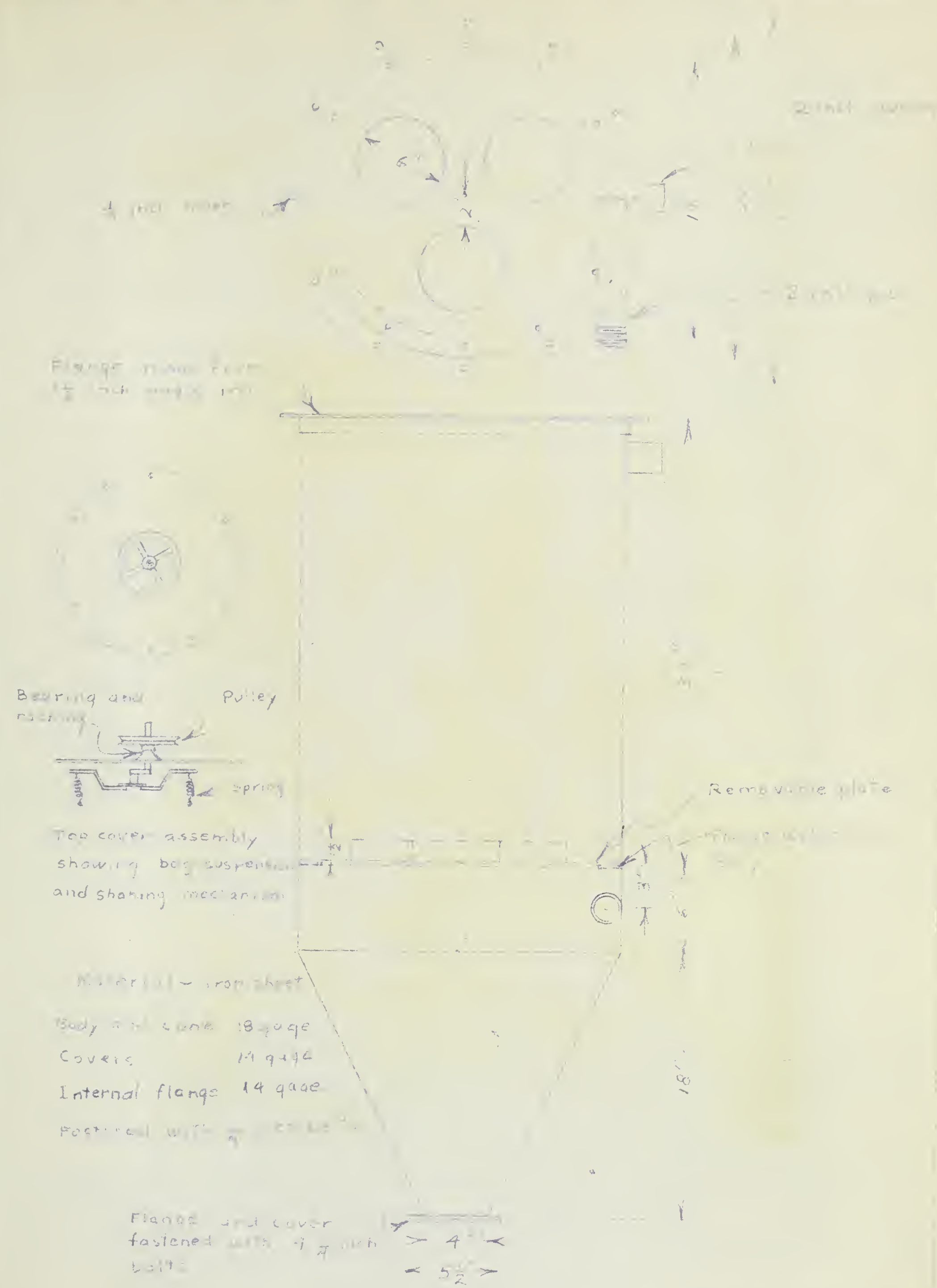


FIGURE XVII

BAG FILTER ASSEMBLY

Scale $\frac{1}{10}$ full size

diameter and 2 feet long (See Figures XVI and XVII). The bags were made of National Filter Media Co. style G201 glass cloth. The tops of the bags were attached by means of coil springs to a shaking mechanism consisting of a three arm spider mounted on a crank having a $2\frac{1}{2}$ inch turning radius. The crank was turned by means of a belt drive from a motor mounted Graham Variable Speed Transmission. The bottoms of the bags were fixed over holes in a horizontal plate (See Figure XVIII). The collected carbon black dropped into a conical storage section.

To simplify operation of the unit all controlling, measuring and indicating devices were grouped together on one control panel (See Figures XIX and XX). The controlling and measuring means for each stream and variable are listed in Table V. A schematic diagram of the complete pilot plant unit is shown in Figure XXI. "Meriam" manometers were used to measure pressures and pressure differentials. The two rotameters used were Fischer and Porter Flowrators. Standard globe, plug-disc gate and needle valves were used for flow and on-off control. Copper tubing 1/4 inch in diameter was used throughout for pressure connections. Orifices were supported in gasket type standard pipe unions. The control panel was built as a complete unit so that if necessary, it could be moved after disconnection of service lines.

The changing specific gravities of the natural gas, off-gas and flue gas, made it necessary to measure their specific gravity periodically. The three sample lines were connected through valves to a common manifold on the control panel. From

the manifold a single line was connected to an Acme Gas Gravity Balance. A compressor was installed on the off-gas sample line to facilitate the collection of a sample for heat of combustion evaluation.

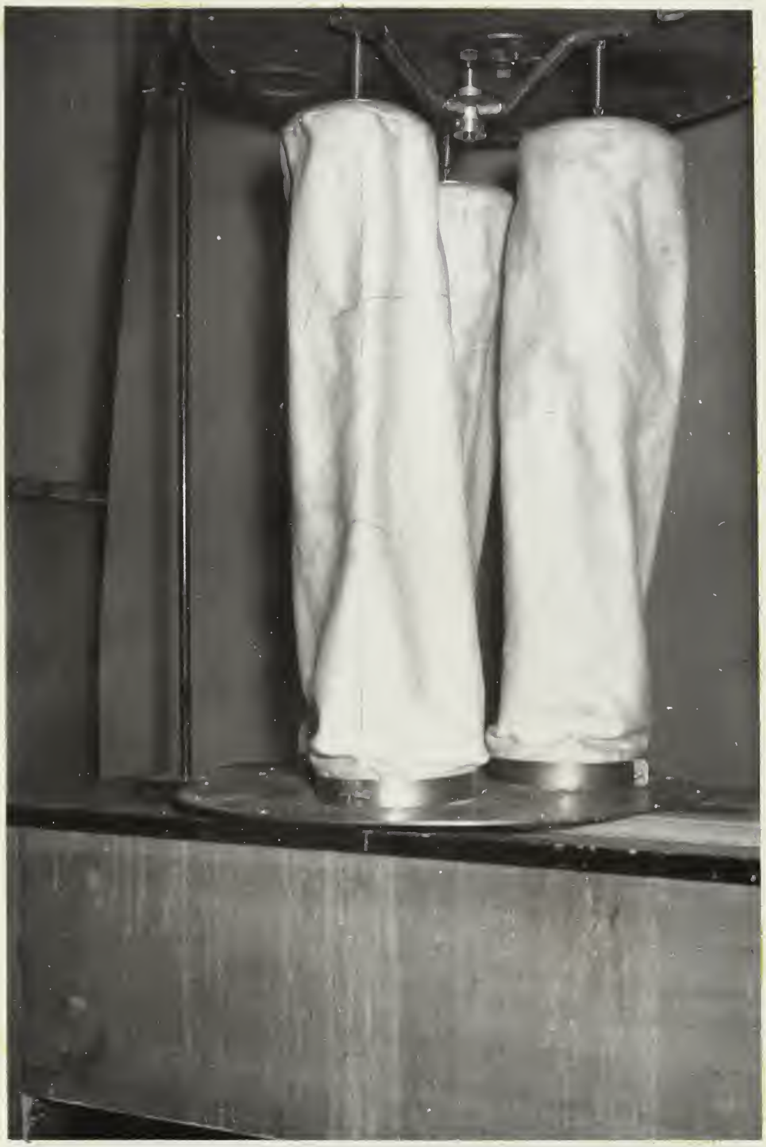


Fig. XVIII. Bag filter mounting

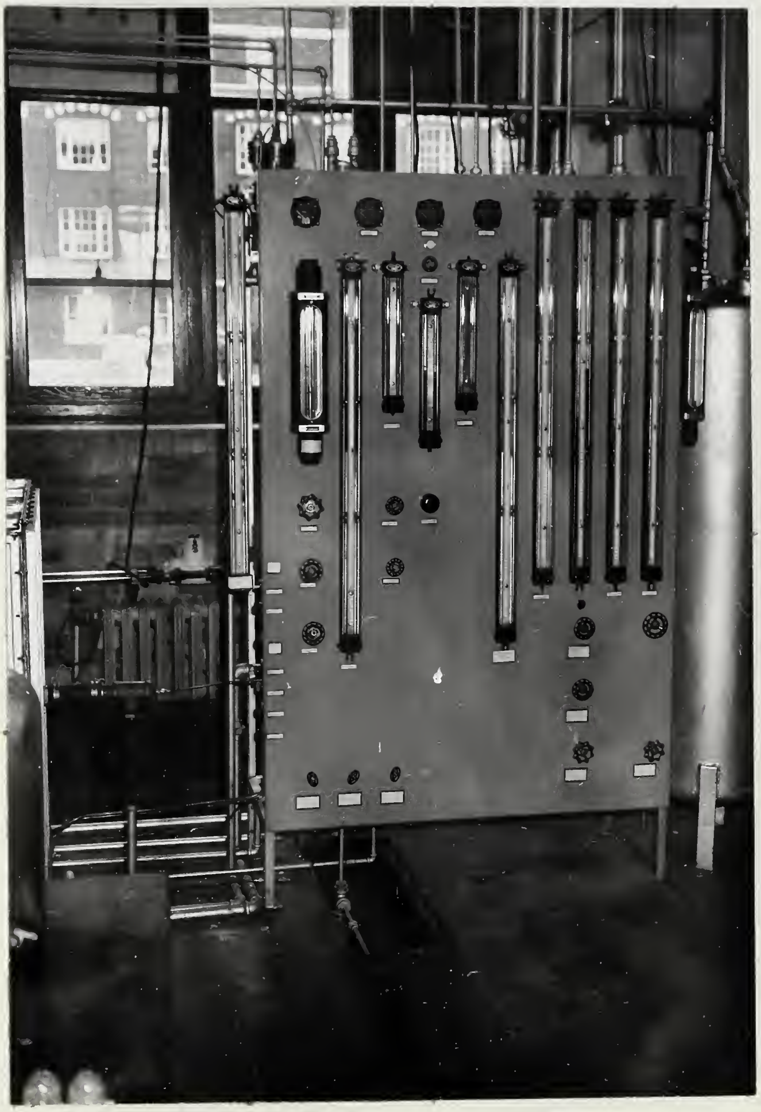


Fig. XIX. Control panel

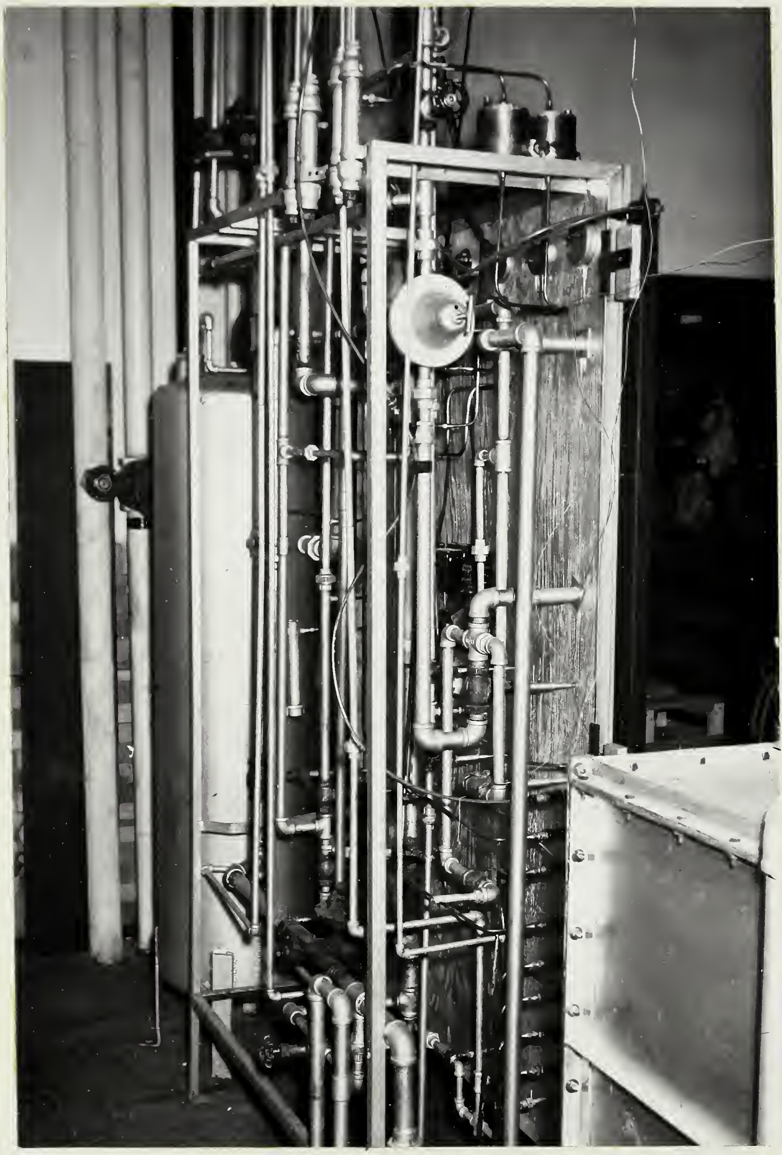


Fig. XX. A view of the back of the control panel

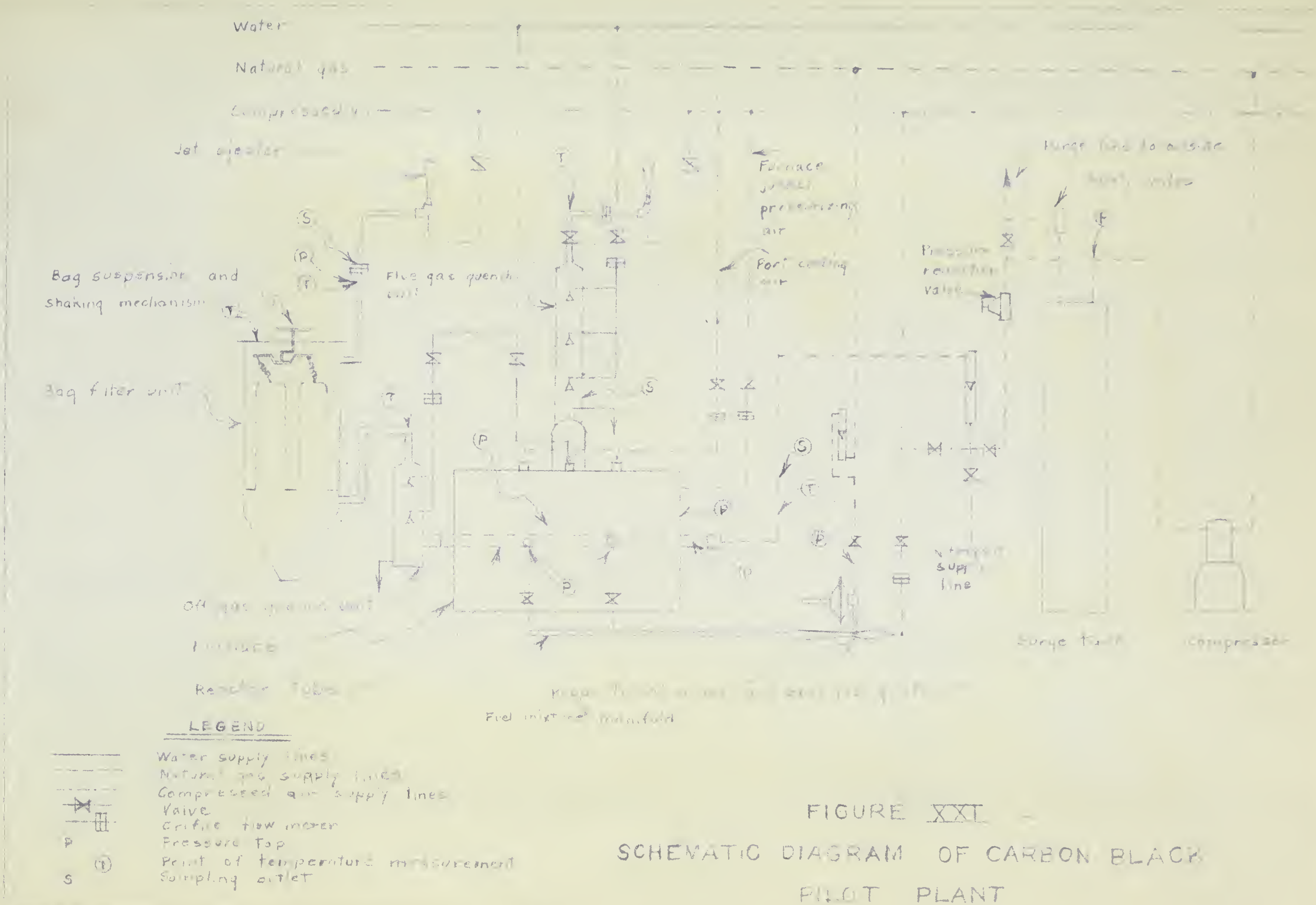


FIGURE XXI

SCHEMATIC DIAGRAM OF CARBON BLACK PILOT PLANT

TABLE V. MEASUREMENT AND CONTROL

Stream, Variable or Unit	FLOW RATE		Temperature	Pressure
	Measurement	Control		
Air supply to proportional mixer	orifice	plug-disc valve	-----	-----
Natural gas supply to proportional mixer	rotameter	automatically proportioned by proportional mixer	-----	water manometer
Fuel mixture to burners	-----	gate valve on each burner	-----	mercury manometer
Flue gas	orifice	-----	continuous indication with thermocouple - millivoltmeter combination, accurate measurement with iron-constantan thermocouple	fire chamber pressure water manometer
Water supply to flue gas quench unit	orifice	plug-disc valve	-----	-----
Water supply to flue gas quench unit offset elbow jacket	-----	globe valve	kept below boiling point of water	-----
Air supply to flue gas jet ejector	-----	globe valve	-----	-----
Furnace fire chamber pressure	-----	-----	-----	water manometer, pressure controlled by jet ejector & butterfly valve

TABLE V. MEASUREMENT AND CONTROL (Cont'd)

Stream, Variable or Unit	FLOW RATE		Temperature	Pressure
	Measurement	Control		
Reactor tube temperature	-----	-----	optical pyrometer, controlled by air-gas ratio and fuel input rate	-----
Furnace jacket pressurizing air	orifice	needle valve	-----	-----
Furnace jacket pressure	-----	-----	-----	water manometer, controlled by pressurizing air rate
Pyrometer port cooling air	orifice	needle valve	-----	-----
Compressor	-----	-----	-----	pressure in surge tank operates pre-set pressure switch
Compressed natural gas to surge tank	------	plug type check valve between compressor and surge tank	-----	pressure gage

TABLE V. MEASUREMENT AND CONTROL (Cont'd)

Stream, Variable or Unit	FLOW RATE		Temperature	Pressure
	Measurement	Control		
Natural gas supply to reactor tube	rotameter	plug-disc valve	mercury thermometer	pressure reduced by reduction valve
Reactor tube air purge	rotameter	globe valve	-----	-----
Reactor tube nitrogen purge	rotameter	globe valve	-----	-----
Reactor tube pressure	-----	-----	-----	water manometer, controlled with jet ejector and gate valve
Off-gas quench unit water supply	orifice	globe valve	-----	-----
Off-gas quench unit temperature	-----	-----	continuous indication with thermocouple-millivoltmeter combination	-----
Bag filter unit	-----	-----	continuous indication with thermocouple-millivoltmeter combination	upstream pressure shown by reactor tube pressure, downstream pressure by water manometer
Off-gas jet ejector air supply	-----	globe valve	-----	-----

VI. EXPERIMENTAL PROGRAM

The experimental program was planned with a view of obtaining the following information:

(1) the effects of the process variables

(2) the optimum operating conditions, for several natural gas compositions, in relation to yields and desirable properties of the carbon black produced

(3) design data
- suitable materials for equipment construction
- equipment capacities
- heat requirements
- special problems encountered
- design recommendations

The process variables may be listed as follows:

(1) reactor tube temperature

(2) retention time of the natural gas in the reactor tube (time of contact)

(3) ratio of reaction gas rate to diffusion gas rate

(4) reactor tube diameter

(5) composition of natural gas feed

The time of contact is a superficial characterization because the rate at which the natural gas is heated to the decomposition is unlikely to have much effect on the yield and properties of the carbon black. Since the natural gas is not heated to the decomposition temperature instantaneously upon entering the reactor tube, the same results should be obtainable

with a high tube temperature and a short time of contact as with a lower temperature and a longer contact time.

The evaluation of the process required data on the following:

(1) Effect of reactor tube temperature on yield, carbon black properties and the composition and heating value of the off-gas.

(2) Effect of contact time on yield, carbon black properties, composition and heating value of the off-gas and reaction gas to diffusion gas ratio.

(3) Effect of reactor tube diameter on the maximum reaction gas to diffusion gas ratio and heat load transmitting capacity.

(4) Effect of varying reactor feed gas composition on yield, carbon black properties and off-gas heating value.

The tube temperature was varied by adjusting the air to gas ratio and the feed rate of the fuel mixture.

The time of contact depended upon the natural gas inlet rate and the reaction gas to diffusion gas rate ratio.

To keep the heating value of the off-gas at a maximum a minimum dilution of the off-gas by diffusing flue gas was necessary. The minimum flue gas diffusion rate required to keep the carbon black from coating out on the wall of the tube was determinable only by trial and error. The best indication of the deposition of carbon black was a rise in tube temperature, all other conditions remaining constant. Oxidation reactions in

the reactor tube were kept to a minimum by maintaining the oxygen content of the flue gas as low as possible.

The heat load transmitting capacity for each tube size was determinable only by trial and error. The many indeterminate factors involved, such as the effect of the hot diffusing flue gas, the thickness and properties of the tube surface gas film, the temperature of the natural gas undergoing endothermic reaction and the degree of radiation absorption of the reacting gas and carbon particles make it impossible to calculate heat transfer rates accurately. Most of the heat energy was transmitted by radiation from the tube walls.

The carbon black yield was determined by a material balance on the process.

The evaluation of the properties of the carbon black samples as reinforcing agents in rubber was to be done by the Rubber Laboratory of the National Research Council at Ottawa. The Research Laboratory of the Columbian Carbon Company at Brooklyn, N.Y. was to do the dimensional evaluation of the carbon black samples.

The composition of the gas supply to the reactor tube was to be varied by recycling part of the off-gas or by the addition of hydrogen. Dilution with hydrogen or recycled off-gas will have an effect on the carbon black particle size and other properties.

The following determinations were necessary:

Natural gas	(1) composition
	(2) specific gravity
	(3) heating value
Off-gas	(1) composition
	(2) specific gravity
	(3) heating value
Flue gas	(1) composition
	(2) specific gravity
Fuel mixture	(1) air to gas ratio (for flame temperature and flue gas composition control)
Carbon black	(1) yield
	(2) evaluation of rubber reinforcing properties

Gas compositions were determined by complete orsat analyses. A Cutler-Hammer continuous calorimeter was used for heating value determinations. Specific gravity was measured with an Acme Gas Gravity Balance. The air to gas ratio in the fuel mixture was determined by measuring the air and gas rates to the proportional mixer.

VII. EXPERIMENTAL RESULTS AND DISCUSSION

No results were obtained in this investigation because each of the three available reactor tubes fractured after a few hours of heating. Several spare reactor tubes were ordered but did not arrive until seven months after the order was placed. Earlier, the construction of the furnace was held up because the burners and the proportional mixer were delivered three months after the promised date of delivery. As a result of these delays, no time was available for further tests.

After some modification, the furnace operated smoothly and good control of reactor tube temperature and pressure and firechamber pressure was possible. A maximum reactor tube temperature, 1388° C, was obtained with a fuel mixture containing about 10% excess air. It is probably possible to raise this temperature by the use of other air to gas ratios and by reducing to a minimum the pyrometer port cooling air rate and the furnace jacket pressurizing air rate.

The Leeds Northrup #8621 optical pyrometer was found to give fairly consistent temperature readings. Radiation absorption by the quartz windows of the pyrometer ports had negligible effect on the temperature readings.

TEST NUMBER I.

A 3 inch inside diameter reactor tube was installed in the furnace. The packing glands on the adaptor plates, through which the tube passed, were packed with slag wool insulating cement.

The furnace was lit and the temperature was brought up to 870° C in three hours using two burners. The other two burners were lit and the temperature was brought up to 1,090° C in two hours. To check the operation of the furnace at a higher chamber pressure, the butterfly valve on the flue gas line was partially closed to increase the firechamber pressure to 10 inches of water. At this pressure it was found that the fuel mixture did not burn evenly, resulting in an oscillation of firechamber pressure. The amplitude of this oscillation was about 8 inches of water at a mean firechamber pressure of 10 inches of water. Soon after this oscillation started, an oscillation in reactor tube pressure was noticed. This indicated a fracture of the tube. The fracture was found to be at a point lying directly beneath the flue gas outlet of the furnace. At first, it was thought that a leak in flue gas quench unit had caused the fracture, but close investigation did not reveal any leaks.

A test carried out on a section of the fractured tube showed the binder used in the construction of the tube, to be plastic at a temperature of 1,400° C. At this temperature the tube had little tensile and crushing strength.

It is believed that the fracture was caused by the tension exerted on the tube by the furnace jacket when the firechamber pressure was increased. The end panels of the furnace jacket were not rigid enough to prevent distortion with increasing pressure.

TEST NUMBER 2.

The second reactor tube, also a 3 inch inside diameter tube, was mounted similarly to the first except that the packing was left out of the packing gland on the inlet side of the tube. This permitted the inlet end of the tube to slide freely through the adaptor plate when thermal expansion took place and when any distortion in the furnace jacket occurred.

The furnace was heated to about 870° C in 4 hours using 2 burners and to 1,340° C in an additional 2 hours using 4 burners. After heating the tube at this temperature for about 2 hours, a fracture was noticed. Removal of the tube from the furnace revealed fractures at each end of the section in the firechamber. To test further the high temperature characteristics of the tube, it was reinstalled in the furnace. The outlet end was fixed to the furnace jacket by the packing in the adaptor plate packing gland and at the other end a turnbuckle and spring arrangement for applying a small compressive force on the tube, was installed. The furnace was heated slowly to 1,260° C and kept at this temperature for 3 hours. The furnace was allowed to cool slowly and the tube was removed. A large number of cracks 1 to 2 inches long running along the tube from each fracture was observed. During the heating of this tube a flow of air (about 400 cu. ft. per hr.) was maintained through the tube to provide a heat load. The tube pressure was kept at 1 to 2 inches below that of the firechamber. It is thought that the longitudinal cracks were caused by the higher temperature at the fracture due to hot flue gas leakage

into the tube.

The fractures occurring at the points of highest temperature gradient indicate the inability of the material from which the reactor tubes were made to withstand thermal shock.

TEST NUMBER 3.

The third tube failed similarly to the second tube. This tube had an inside diameter of 2 inches and a wall thickness of 1/2 inch.

Great care was taken in the installation of this tube to insure that the inlet end of the tube was free to move. The preliminary heating of the furnace was carried out very slowly; the tube temperature reached 480° C in 4 hours, 870° C in 12 hours and 1,390° C in 36 hours.

The fracture in the tube was first noticed after the pressure of the air supply to the proportional mixer had dropped due to the switching off of one of the air supply compressors. In two hours the tube temperature had dropped from 1,390° C to about 1,040° C. The fracture occurred at a point 6 inches from the inlet end of the section in the firechamber.

The tests carried out indicate that the reactor tubes manufactured from Norton Alundum mix number RA1139 are not resistant to thermal shock and are structurally weak at high temperatures.

Before these tubes were ordered, inquiries were made to the Norton Company and they recommended the RA-1139 mixture for our particular application.

Recently enquiries were made to the Carborundum Company, another leading manufacturer of ceramic products. They stated that their aluminum oxide and silicon carbide permeable media would not withstand the high temperatures involved and had low resistance to thermal shock. They also stated that their regular silicon carbide refractory material would withstand the operating conditions but that this material had a low permeability; the diffusion rate was about 0.003 cu. ft. per min. per sq. ft. per inch of water differential. The aluminum oxide tubes used had a permeability such that the diffusion rate was about 0.5 cu. ft. per min. per sq. ft. per inch of water differential for a 1/4 inch thick wall. These tubes probably could not be used because of the difficulties involved in obtaining a high enough pressure differential across the tube wall. However, tests may show that the surface effect of silicon carbide tubes on the thermal decomposition of a hydrocarbon gas is less than the surface effect of aluminum oxide tubes and therefore, a smaller diffusion rate would be necessary to prevent carbon black deposition on the tube wall.

VIII. GENERAL DISCUSSION

The tests outlined in the previous section show that the permeable aluminum oxide tubes tested are unsuitable for high temperature work. The fracturing of the 2 inch inside diameter tube with a 1/2 inch wall suggests that heavy walled tubes may not be the answer to the problem. However, further tests should be carried out on tubes with heavier walls to provide a definite answer. It may be possible to use the available aluminum oxide tubes with 1/4 and 1/2 inch walls if a small compressive force is applied continuously on the tubes. This may be accomplished by fixing one end of the reactor tube and attaching springs between the other end and the furnace jacket.

Permeable silicon carbide tubes, which are at present commercially available, will not withstand high temperatures and thermal shock. Dense silicon carbide tubes able to operate under these conditions do not have a high enough permeability for use in the Pidgeon Process. However, these tubes should be investigated further. It is possible that the surface effect of silicon carbide on the thermal decomposition of hydrocarbon gases is much less than that of aluminum oxide.

A continuous gas generator (17) developed by the Gas Machinery Co. of Cleveland, Ohio, makes use of impermeable silicon carbide tubes 28 feet long. The primary purpose in the development of the generator was the production of high purity hydrogen from the complete thermal decomposition of

hydrocarbon gases. The carbon black, produced as a by-product, was evaluated by carbon black producers and rubber companies who gave it a market value of 5¢ per pound. No mention was made of the deposition of carbon black on the tube walls but apparently this problem was not serious.

The calculations carried out in Appendix D show that by the use of heat exchange equipment and by keeping the dilution with inert gases to a minimum, the off-gas can supply the heat requirements of the process. In the hypothetical case chosen about 82 Btu are available from the off-gas produced by the decomposition of 60% of each cubic foot of entering methane. About 34 Btu at 1,400° C are required for the thermal decomposition of 60% of each cubic foot of entering methane.

Several other methods for the production of carbon black from natural gas which would provide good control of temperature and contact time are listed below.

(1) A furnace in which compartments are separated by permeable refractory plates could be used. Heat for the thermal decomposition of hydrocarbons would be supplied by combustion in alternate compartments. Diffusion of hot flue gases through the permeable refractory plates from the combustion compartments to the reaction compartments would prevent the deposition of carbon black on the plates. A pressure differential across the plates would provide the driving force for gas diffusion.

(2) Another method would involve the use of glow tubes to heat a decomposition reaction chamber. Combustion in

these permeable refractory tubes would supply the heat and the diffusion of flue gases through the walls of the tubes would prevent deposition of carbon black.

(3) A variation of the furnace thermal process could also be used. This method would have the advantage of a constant reaction chamber temperature. The furnace would be compartmented by thin refractory walls. Combustion in alternate compartments would supply the heat requirements. The carbon black deposited in the reaction compartments would be burned periodically by the injection of air.

This investigation of the Pidgeon Process on a pilot plant scale has not been carried out far enough for a definite conclusion to be reached regarding the feasibility of the process.

Silicon carbide and heavy walled aluminum oxide tubes should be investigated. This work can be carried out at a reasonable cost with the present equipment.

BIBLIOGRAPHY

(1) Anonymous, "A Study of Small Diameter Gas Glow Tubes", Research Bulletin Number 56, American Gas Association Laboratories, Cleveland, Ohio, October, 1950.

(2) Anderson, R.B., and Emmett, P.H., J. Applied Phys., 19, 367 (1948)

(3) Braendle, H.A., Colloid Chemistry, 6, 408 (1946)

(4) Braendle, H.A., Sweitzer, C.W., and Steffen, H.C., Rubber Age (N.Y.), 64, 708 (1949)

(5) Bureau of Mines, Report of Investigations 4695, United States Department of the Interior, May, 1950.

(6) "Canada Year Book", Dominion Bureau of Statistics, Ottawa, 1950.

(7) Clark, G.S., "Applied X-rays", McGraw-Hill Book Company, Inc., New York, 1932

(8) Columbian Carbon Company Research Laboratories, "Columbian Colloidal Carbons", Vol. II, New York, 1940

(9) Columbian Carbon Company Research Laboratories, "Columbian Colloidal Carbons", Vol. III, New York, 1942

(10) Coward, H.F., and Wilson, S.P., J. Chem. Soc., 115, 1380 (1919)

(11) Drogin, I., "Development and Status of Carbon Black", United Carbon Company, Inc., Charleston, West Virginia, 1947

(12) Egloff, G., "Reactions of Pure Hydrocarbons", Reinhold Publishing Corporation, New York, 1937

(13) Emmett, P.H., and DeWitt, T., Ind. Eng. Chem., Anal. Ed., 13, 28 (1941)

(14) Kirk, R.E., and Othmer, D.F., "Encyclopedia of Chemical Technology", Vol. 3, pp. 52, The Interscience Encyclopedia, Inc., New York, 1947

(15) Lewis, G.C., and Mantell, C.L., "Industrial Carbon, Its Elemental, Adsorptive and Manufactured Forms", D. Van Nostrand Company, Inc., New York, 1945

(16) Lewis, G.N., and Randall, M., "Thermodynamics and Free Energy of Chemical Substances", McGraw-Hill Book Company, New York, 1923

(17) Madenheim, H., "Continuous Gas Generator Shows Promise In Base Load and Standby Operations", Reprint, American Gas Journal, January, 1950.

(18) Moore, R.L., Ind. Eng. Chem. 24, 21 (1932)

(19) Neal, R.O., and Perrott, G. St. J., Bureau of Mines Bulletin Number 1932 (1922)

(20) Parks, G.S., and Huffman, H.M., "Free Energies of Some Organic Compounds", 99, American Chemical Society Monograph No. 60, Chemical Catalog Co., Inc., New York, 1932

(21) Perry, J.H., "Chemical Engineers' Handbook", 2nd. ed., pp. 1000, McGraw-Hill Book Company, New York, 1941

(22) Perry, J.H., "Chemical Engineers' Handbook", 2nd. ed., pp. 951, McGraw-Hill Book Company, New York, 1941

(23) Perry, J.H., "Chemical Engineers' Handbook", 2nd ed., pp. 2406, McGraw-Hill Book Company, New York, 1941

(24) Perry, J.H., "Chemical Engineers' Handbook", 2nd ed., pp. 2012, McGraw-Hill Book Company, New York, 1941

(25) Pettyjohn, E.S., National Petroleum News, 38, 596 (1946)

(26) Pidgeon, L.M., Canadian Journal of Research, B, 13, 351 (1935)

(27) Smith, W.R., Thornhill, F.S., and Bray, R.I., Ind. Eng. Chem., 33, 1303 (1941)

(28) Steffen, H.C., Indian Rubber World, 120, 60 (1949)

(29) Stokes, C.A., Dannenberg, E.M., Ind. Eng. Chem. 41, 381 (1949)

(30) Sweitzer, C.W., Braendle, H.A., India Rubber World, 107, 468 (1943)

(31) Sweitzer, C.W., and Goodrich, W.C., Rubber Age (N.Y.) 55, 469 (1944)

(32) Sweitzer, C.W., Goodrich, W.C., and Burgess, W.S., Rubber Age (N.Y.) 65, 651 (1949)

(33) Twiss, D.F., Trans. Inst. Rubber Ind., 407 (1930)

(34) Uhlinger, R.H., U.S. Patent No. 1,478,730 (1923)

(35) Weigand, W.B., Can. Chem. and Process Ind., 25, 579 (1941)

(36) Weigand, W.B., Ind. Eng. Chem. 29, 953 (1937)

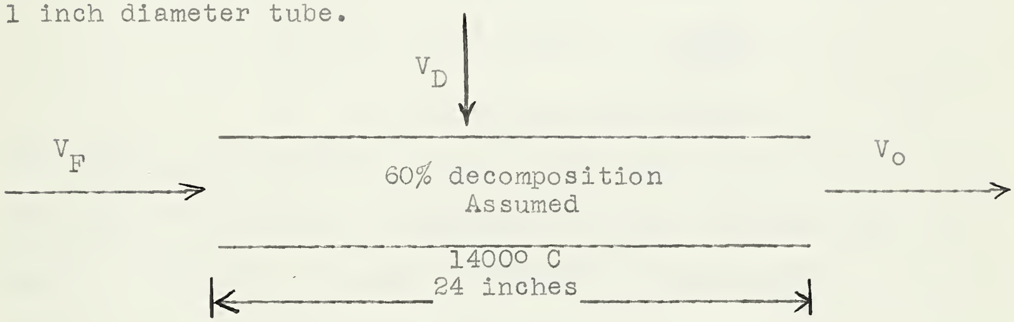
(37) Weigand, W.B., Personal communication, 1949

APPENDIX A

EQUIPMENT DESIGN CALCULATIONS

(1) Calculation of Heat Requirements

The following calculation of the heat requirements for the 3 inch reactor tube is based on 0.1 sec. retention time, 60% decomposition, and a flue gas diffusion rate such that the ratio of inlet to diffusion volume is 0.6 for the 1 inch diameter tube.



V_F = natural gas feed rate cu. ft. per sec.

V_D = flue gas diffusion rate cu. ft. per sec.

V_o = off-gas rate cu. ft. per sec.

For 1 inch diameter tube 15 inches long

$$\frac{V_F}{V_D} = 0.6$$

For 3 inch diameter tube 24 inches long (length for diffusion)

$$V_F = 0.6 \times \frac{9}{3} \times \frac{15}{24}$$

$$= 1.13$$

If

$$V_F = 1$$

$$V_o = 1 \times 1.6 + \frac{1}{1.13}$$

$$= 2.49$$

Average gas volume in tube per second

$$= \frac{(1 + 2.49)}{2} V_F$$

$$= 1.74 V_F$$

Gas velocity at 0.1 seconds time of contact

$$= 20 \text{ ft./sec.}$$

$$V_F = \frac{20 \times 0.049}{1.74}$$

$$= 0.563 \text{ ft}^3\text{/sec. @ } 1{,}400^\circ \text{ C}$$

$$V_o = 1.6 \times 0.563 + \frac{0.563}{1.13}$$

$$= 1.4 \text{ ft}^3\text{/sec. @ } 1{,}400^\circ \text{ C}$$

The feed rate at 60° F is 353 cu. ft. per hour

The heat of formation of methane is given by Parks (20) as

$$\Delta H = -15{,}450 - 11.1T + 0.0081T^2 - 0.0000012T^3$$

where ΔH = calories per gram mol

T = temperature °K

ΔH @ 1,400° C = -16,960 calories per gram mol

Converting to Btu per cu. ft. of methane @ 60° F

ΔH = -80.5 Btu per cu. ft. methane

The heat required for 60% decomposition at a contact time of 0.1 seconds is

$353 \times 0.6 \times 80.5$ = 17,070 Btu per hour @ 1,400° C

Heat is also required to preheat the incoming gas to the decomposition temperature.

For the purpose of calculating approximate heat losses by conduction from the furnace, a cylindrical cross-section was assumed.

Firechamber diameter	13 inches
Firebrick thickness	4½ inches
Insulating brick thickness	4 inches
Block insulation thickness	3 inches
Length	3 feet
End wall (assume circular shape)	
Diameter	2 feet
Firebrick thickness	4½ inches
Insulating brick thickness	2½ inches
Insulation	2 inches

Fire brick $k = 2.7$ Btu/(hr.)(sq. ft.)(°F/ft.) (22)

Insulating brick $k = 0.15$ Btu/(hr.)(sq. ft.)(°F/ft.) (22)

Block insulation $k = 0.050$ Btu/(hr.)(sq. ft.)(°F/ft.) (22)

Air film coefficient $h = 0.86$ Btu/(hr.)(sq. ft.)°F (22)

The resistance to heat transfer, of the sheet metal furnace case will be small and may be disregarded.

The overall coefficient was calculated to be 0.162 based on the logarithmic mean area of the cylinder (17.6 sq.ft.) Assume the furnace firechamber walls to be at 2,600° F and the room air temperature to be 80° F

For the walls

$$
\begin{aligned}
q &= U\,A_{lm}\,\Delta T \\
&= 0.162 \times 17.6\,(2600 - 80) \\
&= 7{,}200 \text{ Btu per hour}
\end{aligned}
$$

For the ends

$$
\begin{aligned}
U &= 0.162 \\
q &= 0.165 \times \frac{3.14 \times 9}{4}\,(2600 - 80) \times 2 \\
&= 5{,}880 \text{ Btu per hour}
\end{aligned}
$$

Approximate heat loss by conduction through brickwork is 13,040 Btu per hour. With an overdesign factor of over 3, the heat requirement will be approximately 100,000 Btu per hour.

(2) Design of Flue Gas Quench Unit

Natural gas requirement (980 Btu per cubic feet gas) is approximately 120 cu. ft. per hour.

Air requirement is approximately 1,000 cu. ft. per hour.

Cubic feet of flue gas to be cooled 1,120 cu. ft. per hour.

Base design on 1,400 cu. ft. per hour @ 60° F of flue gas at 2,400° F.

Area for heat transfer in offset elbow cooling jacket is approximately 1.52 sq. ft.

Flue gas composition for stoichiometric combustion of methane

	Mol Fr.
CO_2	0.092
H_2O	0.182
N_2	0.726
	1.000

Calculation of approximate specific heat of flue gas

Component	C_p Btu per lb. mol @2000° F	Mol Fr.	Fr. C_p	Mol Wt.	Fr. Mol Wt.
CO_2	12.10	0.092	1.1	48	4.42
H_2O	9.33	0.181	1.7	18	3.26
N_2	7.57	0.726	5.5	29	20.3
		C_p =	8.3	Mol Wt. =	27.98

Mass Rate G of flue gas $= \dfrac{1400 \times 2.8}{379 \times 0.111}$

= 935 lb. per hr. per sq. ft.

= 0.26 lb. per hr. sec. per sq. ft.

Using the Dittus-Boelter Equation the overall heat transfer coefficient was calculated to be approximately 1 Btu per (hr)(sq. ft.)(^{o}F)

$$q = UA\Delta T$$

$$= 1 \times 1.52\ (2400 - 180)$$

$$= 3,380 \text{ Btu per hr.}$$

Total quantity of heat to be removed to cool the flue gas to 400° F

$$= 1400 \times 8.3\ (2400 - 400)$$

$$= 61,400 \text{ Btu per hr.}$$

Heat to be removed by water spray

$$= 61,400 - 3,380$$

$$= 58,020 \text{ Btu per hr.}$$

Water required for cooling

$$= \frac{58,000}{970}$$

$$= 60 \text{ lb. per hr.}$$

Calculation of quench unit spray chamber volume

$$q = ha\Delta T \quad dV$$

$$ha = 40 \text{ Btu per (hr.)(cu. ft.)}(^{o}\text{F}) \qquad (21)$$

$$V = \frac{58,020}{40 \times 2000}$$

$$= 0.725 \text{ cu. ft.}$$

Height of spray chamber $= \dfrac{0.725}{0.111}$

$$= 6.52 \text{ ft.}$$

A spray chamber height of 5½ feet was used because of clearance limitations.

The water sprayed (21.5 U.S. gals. per hr.) in was approximately three times the water evaporated.

(3) Design of Off-Gas Quench Unit

The approximate composition of the off-gas was calculated from rates for a contact time of 0.1 sec. and 60% decomposition.

Component	Mol Fr.	Mol Wt.	Fr. Mol Wt.	C_p Btu/Mol °F @ 2000° F	Fr. C_p
CH_4	0.16	16	2.56	13.5	2.16
H_2	0.48	2	0.96	7.28	3.49
CO_2	0.034	44	1.50	12.46	0.42
H_2O	0.068	18	1.22	9.70	0.66
N_2	0.258	28	7.22	9.72	0.99
		Mol Wt.	13.46	C_p	8.72

Off-gas rate for 0.1 sec. contact time and inlet to diffusion gas rate ratio of 1.13 is approximately 2.5 lb. mols per hr.

Quantity of heat to be removed to cool the off-gas from 2,600° F to 400° F

$$= 2.5 \times 8.72\ (2600 - 400)$$

$$= 48{,}000 \text{ Btu per hr.}$$

$$q = ha \quad TdV$$

$$h_a = 40 \text{ Btu per (hr.)(cu. ft.)(°F)}$$

$$V = 0.545$$

Height of quench unit spray chamber

$$= \frac{0.545 \times 4 \times 144}{3.14 \times 36}$$

$$= 2.78 \text{ ft.}$$

Water required for quenching

$$= \frac{48{,}000}{970}$$

$$= 49.5 \text{ lb. per hr.}$$

Water sprayed in = 10 U.S. gals per hr.

APPENDIX B

OPERATING TECHNIQUE

(1) Turn off all flow rate control valves on the instrument panel.

(2) Turn on all service main valves.

(3) Switch on flood warning system.

(4) Turn on offset elbow jacket cooling water.

(5) Open fully the gate valves on the fuel mixture lines to the burners on the pyrometer port side of the furnace. Close the valves on the fuel mixture lines to the other two burners.

(6) Unscrew the lighting port plug on the pyrometer port side of the furnace and pull out the ceramic plug.

(7) Turn on the furnace jacket pressurizing air and the pyrometer port cooling air to give differentials of about 5 and 4 inches of mercury respectively.

(8) Turn on the flue gas quench unit water spray. The differential across the orifice should be about 20 cm. of carbon tetrochloride under water.

(9) After making sure that the plug cock on the natural gas supply line to the proportional mixer is closed, open the air supply valve to the proportional mixer until a pressure differential across the orifice of about 4 cm. is obtained.

(10) Open completely the mixture control needle valve on the proportional mixer.

(11) Insert the spark gap wand into the lighting port and switch on the induction coil.

(12) Open the plug cock on the natural gas supply line to the proportional mixer.

(13) If the furnace does not light within about 30 seconds, close the gas supply plug cock and allow the furnace to be purged with air before attempting to light up again. This procedure is necessary to prevent ignition of the large volume of explosive mixture in the furnace.

(14) When the furnace is lit, adjust the flue gas ejector air supply to obtain a vacuum of about 2 inches of water in the furnace firechamber.

(15) Replace the plugs in the lighting port.

(16) Allow the furnace to warm up slowly up to 1,600° F over a period of 2 to 3 hours at the original settings and then adjust the fuel mixture to the proper proportions for stoichiometric combustion.

(17) Turn on the reactor tube air purge until a scale reading of 2 is obtained on the flowrator.

(18) Allow the furnace to warm up for 6 to 8 hours and then turn on the other two burners one at a time. Adjust the air rate to the proportional mixer to obtain a differential of about 12 cm. of mercury. Adjust the mixture pressure at the burner heads to the same value by means of the gate valves on the manifolds.

(19) Adjust the quench water rate to keep the quenched flue gas temperature at about 200° C.

(20) Adjust the offset elbow cooling jacket water rate so that the water comes out at about 200° F.

(21) Adjust the pyrometer port cooling air rate to get a differential of 6 inches of mercury.

(22) Adjust the furnace jacket pressurizing air rate until the jacket pressure is just slightly above the firechamber pressure.

(23) When the operating temperature has been reached, turn off the reactor tube air purge and calibrate the reactor tube for diffusion rate vs. pressure differential across the tube wall using a 1/4 inch orifice installed in the off-gas exhaust line. Vary the pressure differential across the tube wall by adjusting the air supply to the flue gas and off-gas jet ejectors.

(24) Flush out the natural gas supply surge tank by opening the purge line valve and running the compressor.

(25) Close the purge line valve and let the pressure in the surge tank build up until the compressor is switched off by the pressure switch. The pressure switch should be set to maintain a pressure of 40 to 60 psi in the surge tank.

(26) Purge the reactor tube and system with nitrogen to prevent the possibility of explosion when the natural gas is introduced.

(27) Set the natural gas rate to the reactor tube at the required valve and adjust the firechamber and reactor tube pressures

by means of the jet ejectors until the required pressure differential is obtained.

(28) Turn on the off-gas quench water if required. It was found that the off-gas was cooled sufficiently by heat losses in the quench unit making it necessary to use water spray.

(29) Keep a constant check on reactor tube temperatures. A rise in temperature may indicate a coating out of the carbon black on the tube wall. If carbon black has coated out, purge the system with nitrogen and burn the carbon black by introducing air to the reactor tube.

(30) Turn on the bag filter shaking mechanism intermittently to shake out the collected carbon black.

(31) On completion of the run, remove the carbon black by taking off the blanking plate on the bottom of the conical storage section of the bag filter unit.

An oscillation in the zero gas governor of the proportional mixer may start under certain conditions. This can be stopped without shutting down the furnace by cutting down the air rate to the furnace until a differential of about 5 cm. is obtained and opening wide the mixture control needle valve on the proportional mixer. When the oscillation has stopped, increase the air rate and slowly adjust the mixture control needle valve until the proper air to gas ratio is obtained.

The line filters on the quench water supply lines should be cleaned before each run.

APPENDIX C

EQUIPMENT CONSTRUCTION PROBLEMS

This section was included to acquaint the reader with some of the problems encountered in the design, construction and operation of the equipment and how these problems were solved.

Special refractory shapes such as streamlining liners for the burner tunnels and angle bricks for supporting the dome of the furnace, were made from plastic firebrick. These special shapes appear to have stood up very well under high temperature service. Expansion joints were not employed in the brickwork but no serious cracks have developed so far.

The silicon carbide plates used to prevent flame impingement on the reactor tube were mounted in slots milled in the brickwork. Space was provided for the expansion of the plates. The slots were milled in the bricks with a 1/2 inch "carboloy" masonry drill.

The holes for the pyrometer ports were drilled through the brickwork, with a special cutter, after the construction of the dome. The cutter consisted of a 4 inch section of 1 inch diameter iron pipe with 1/2 inch teeth cut into one end. The cutter was mounted on a 1/2 inch diameter rod. The teeth on the cutter were case hardened in an acetylene atmosphere after heating to yellow heat. A jig made out of iron pipe was used in the drilling of the holes to make certain that the axis of the holes intersected the centerline of the reactor tube. Before

drilling with the cutter, 1/4 inch guide holes were drilled, using the jig and a 1/4 inch "carboloy" masonry drill. 1 inch inside diameter alundum tubes were cemented into the brickwork to act as liners for the pyrometer ports.

The furnace lighting ports were drilled and lined in a similar manner.

Several methods, including a gas flame and a hot filament, were tried as a means of lighting the furnace. The use of an electric arc was the only successful method.

A spark gap mounted on a length of 1/4 inch pipe provided the arc. A piece of 14 gauge copper wire insulated with a length of porcelain thermocouple insulator running through the pipe provided the other electrode. High tension current was obtained from a Model T Ford ignition coil hooked up to a six-volt storage battery.

The flue gas outlet of the furnace was made by chipping out a hole in the dome and lining it with a 12 inch length of alundum tube, having a 4 inch inside diameter and a 1/2 inch wall thickness. The tube was cemented in so that it extended above the brickwork into the flue gas quench unit. The annular space between the tube and the walls of the well in the top of the steel furnace case was packed with slag wool insulating cement.

In the first firing of the furnace, overheating of the pyrometer port quartz window mountings and certain spots on the furnace case, was encountered. This was found to be due

to leakage of hot flue gases into the space between the furnace case and the brickwork. Leaks in the steel furnace case and the above atmospheric pressure in the firechamber increased the leakage. This condition was remedied by continuously blowing compressed air into the furnace case to maintain the pressure in it above the firechamber pressure.

Compressed air was also blown into the pyrometer ports just below the quartz window mountings to assist in keeping the quartz windows cool and clean.

Preliminary heating runs with the furnace revealed uneven burning in the firechamber with a resulting oscillation in firechamber pressure. At the higher firechamber pressures, the pressure varied as much as 10 cm. of water. At the higher fuel rates, the pressure drop in the flue gas exhaust system prevented lowering of the firechamber pressure, making an evacuation system necessary. The jet ejectors described in the equipment design section and shown in Figure III, were built after considerable experimenting with throat diameters, wall to axis angles and jet nozzle position. The installation of these ejectors on both the flue gas and off-gas exhaust lines, made possible good control of firechamber and reactor tube pressures. The lower firechamber pressure eliminated most of the pressure oscillation.

The danger of explosion of the fuel mixture in the cold furnace when starting up, made it necessary to prevent any leakage of natural gas into the firechamber. The proportional mixer does not operate properly at low air rates such as are

encountered when turning on the air supply to the mixer. This made it necessary to cut off the gas supply until the air rate reached the proper value. A plug cock was installed in the gas supply line to permit rapid turning on of the gas supply.

Under certain conditions an oscillation was set up in the diaphram of the zero gas governor of the proportional mixer, resulting in a continuously varying air to gas ratio and uneven burning. This condition was remedied by the installation of a 1/64 inch orifice in the 1/4 inch diameter pressure feedback line between the throat of the proportional mixer venturi and the underside of the zero gas governor diaphram.

The design of the manifold used to distribute the fuel mixture from the proportional mixer to the burners resulted in an uneven supply to the respective burners. Gate valves to adjust the fuel mixture pressure at the burner head were installed to equalize distribution. The burner head pressure was measured with a mercury manometer.

The flue gas quench unit sump was drained through a 3/4 inch pipe drainage system, having a hydraulic leg of 20 inches. Preliminary tests showed the draining capacity to be too small because of air locks in the vertical leg. This was eliminated by running a 1/4 inch pipe from the top of the vertical leg back to the spray chamber at a point above the sump. A flood warning system (described in the design section and shown in Figure X) was thought necessary because any water draining into the firechamber would cause serious damage.

The original reactor tube was permeable along its entire length. Since diffusion of flue gases into the reactor tube was required only along the hot section in the firechamber, the tube was made impervious at each end by painting it with a sodium silicate solution. A 23 inch section was left permeable (See Figure V).

The inlet end of the reactor tube was connected to the natural gas supply line by a length of rubber hose. This end remained cool enough to prevent scorching of the rubber. The outlet end of the reactor tube was cemented into a stainless steel collar connected to the off-gas quench unit by a special flange connection (See Figure XIII).

A clearance of 1/8 inch was provided between the brickwork in the ends of the furnace and the reactor tube to ensure free movement of the tube during thermal expansion. The joints between the reactor tube and the adapter plates of the furnace case were sealed by means of packing glands. The annular space formed by the reactor tube and a section of pipe brazed to the adaptor plate was packed with an insulating cement (slag wool). The packing was compressed by a follower held down by 4 studs. The packing at the inlet end was left loose to allow the tube to move freely during expansion.

The Curtis compressor used to compress the gas supply to the reactor tube was of the type ordinarily used for compressing air. It was necessary to plug several holes in the head and base of the compressor to prevent gas leakage. To carry off any gas blown past the piston into the crankcase,

the crankcase was vented to the outside of the building through a 1/4 inch pipe.

A safety pressure relief valve installed on the gas supply surge tank was also vented to the outside. The surge tank was also provided with a blowdown line to the outside of the building so that gas in the tank at the completion of a run could be bled off.

The compressor was of the splash lubrication type making an oil separator necessary to prevent contamination of the compressed gas by oil. An oil removal unit consisting of a 2 foot piece of 4 inch pipe, packed with 1/4 inch raschig rings, glass wool and granulated charcoal, was installed. Tests with this type of oil removal filter revealed that practically all the oil vapor was removed.

The filter bags of the bag filter unit were shaken by the motion of the crank mounted on a shaft passing through the top of the filter housing. The top of a globe valve brazed to the filter housing acted as the bearing and seal for the shaft. The springs used to attach the bags to the arms of the spider, gave an extra snap to the shaking motion and relieved some of the strain on the bags. The springs were attached to bolts passing through the tops of the bags and two dished aluminum washers. The bottoms of the bags were attached by clamps to flanges welded to a fixed plate in the filter housing.

Pressures not requiring continuous measurement were led through plug cocks to a common manifold connected to a manometer of the correct pressure range.

Continuous temperature readings of the quenched flue gas and the off-gas were obtained by installing thermocouple type aircraft engine cylinder temperature indicators.

To measure accurately the pressure differential (a maximum of 3 inches of water) across the orifice in the off-gas exhaust line, a multiplying manometer was required. The use of an inclined water manometer would have necessitated its mounting on a separate panel. A vertical two fluid type of multiplying manometer was used. Airtight brass pots with an inside diameter of 3 inches were connected to the top of a manometer. The manometer tubing had an inside diameter of about 0.13 inches. The two fluids used were water and toluene. A multiplication of about 7.3 was obtained. The manometer was calibrated against an inclined water manometer. All orifices and rotameters were calibrated before installation.

Originally a calibrated conductivity cell was to be used to measure the gas to air ratio in the fuel mixture, however, this method had to be abandoned in favor of direct measurement of the gas and air stream because of wide variations in the natural gas composition.

APPENDIX D

CALCULATION OF HEAT AVAILABLE FROM OFF-GAS

The calculation of the heat available from an off-gas of the composition shown in Column 1, Table IV, page 23, was carried out similarly to the calculations shown in the following example:

Calculation of Heat Available at 1,400° C from the Combustion of the Off-Gas Produced from 1 Cubic Foot of Methane.

Conditions - 60% decomposition

- Reaction gas to diffusion gas ratio = 1.13

Composition of flue gas for stoichiometric combustion of methane.

$$CH_4 + 2O_2 + 7.5\ N_2 \longrightarrow CO_2 + 2H_2O + 7.5\ N_2$$

Component	Mols	Mol. Fr.
CO_2	1	0.09
H_2O	2	0.20
N_2	7.5	0.71
	10.5	1.00

Composition of off-gas produced under above conditions.

$$CH_4 \longrightarrow C + 2H_2$$

Basis: 100 mols of methane feed

Component	Mols	Mol. Fr.
CH_4	40	0.16
H_2	120	0.48
CO_2	8	0.03
H_2O	17.3	0.07
N_2	63.1	0.26
		1.00

Calculation of Heat of Combustion

Component	Mol Fr.	Heat of Comb. Btu/Mol	Fr. Heat of Comb. Btu/cu. ft.
CH_2	0.161	346,000	147
H_2	0.483	104,100	133
CO_2	0.032	---	---
H_2O	0.069	---	---
N_2	0.254	---	---

Off-gas heating value = 280 Btu/cu.ft.

Calculation of flue gas composition and specific heat for the stoichiometric combustion of the off-gas

$$CH_4 + 2O_2 + 7.5\ N_2 \longrightarrow CO_2 + 2H_2O + 7.5\ N_2$$

$$H_2 + \tfrac{1}{2}O_2 + 1.88\ N_2 \longrightarrow H_2O + 1.88\ N_2$$

Basis: 100 mols off-gas

Component	Mols	Mol Fr.	C_p (Mean 60-3000°F) Btu/mol (°F)	Fr. C_p Btu/cu. ft. (°F)
CO_2	19.3	0.06	12.76	0.002
H_2O	87.4	0.25	10.04	0.007
N_2	237.1	0.69	7.85	0.014
	343.8	1.00		0.023

Mean specific heat (60 - 3000° F) for the flue gas is 0.023 Btu/cu. ft.(°F)

For 1 cu. ft. of methane entering the reactor tube, there are 2.48 cu. ft. of off-gas and 3.43 cu. ft. of flue gas when the off-gas is burned with the volume of air required for stoichiometric combustion.

$$\text{Theoretical flame temperature} = \frac{\text{heat of combustion} + \text{sensible heat in fuel} + \text{sensible heat in air}}{\left\{\begin{array}{l}\text{total quantity}\\ \text{of combustion}\\ \text{products}\end{array}\right\} \times \left\{\begin{array}{l}\text{their mean}\\ \text{specific heat}\end{array}\right\}}$$

Let sensible heat = 0 at 60° F

$$\text{T. F. T.} = \frac{280}{3.43 \times 0.023} + 60$$

For 60% decomposition of 1 cu. ft. of methane into carbon and hydrogen at 1,400° C (2552° F) 34 Btu are required (See Appendix A-1).

The theoretical heat available at 1,400° C from the volume of off-gas produced by the decomposition of 60% of 1 cu. ft. of methane (inlet gas/diffusion gas = 1.13)

$$= 3.43 \times 0.023\ (3600 - 2552)$$

$$= 82.7\ \text{Btu}$$

The theoretical flame temperature would not be reached in practice because part of the heat would be used up in the decomposition of H_2O and CO_2.

APPENDIX E

CARBON BLACK BIBLIOGRAPHY

(1) Carbon Black Properties

Amon, F.H., "Experiences with a Direct Accelerator-Adsorption Test", Ind. Eng. Chem., 24, 579 (1932)

Amon, F.H., "Identification of Carbon Black by Surface Area Measurements", Ind. Eng. Chem., Anal. Ed. 15, 256 (1943)

Anonymous, "New Method Mixes Liquid Rubber with Carbon Black", Oil and Gas Journal, 43, 118 (16 Sept, 1944)

Anonymous, "Uniform Carbon Black Nomenclature", India Rubber World, 112, 48, 488 (1943)

Anonymous, "Carbon Black Nomenclature", Rubber Age, 60, 538 (1945)

Anonymous, "Physical Properties and Behavior in Rubber of Continental Carbon Blacks", Report R1, Continental Carbon Company, New York, June 1, 1943

Anonymous, "Carbon Black Manual", Wilco Chemical Co., New York, 1945

Anonymous, "Particle Size and Shape of Colloidal Carbons as Revealed by the Electron Microscope", Columbian Colloidal Carbons, Vol. 2, Columbian Carbon Co., New York, 1940

Anonymous, "Surface Area of Colloidal Carbons", Columbian Colloidal Carbons, Vol. 3, Columbian Carbon Co., New York, 1942

Anonymous, "Carbon Reinforcement of Buna S (GR-S), Columbian Colloidal Carbons, Vol. 4, Columbian Carbon Co., New York, 1943

Anonymous, "Carbon Reinforcement of Neoprene GN", Columbian Colloidal Carbons, Vol. 6, No. 1, Columbian Carbon Co., New York, 1945

Bartell, F.E., "Adhesion Tension Values of Different Types of Carbon Black Against Water and Against Benzene", Ind. Eng. Chem., 21, 1102 (1929)

Beaver, D.J., "Effect of Various Types of Carbon Black on Certain Physical Properties of Rubber Compounds", Ind. Eng. Chem., 20, 817 (1928)

Beaver, D.J. and Keller, T.P., "Carbon Black", Ind. Eng. Chem., 20, 817 (1928)

Biscoe, J., "X-ray Study of Carbon Black", J. App. Phys., 13, 364 (1942)

Braendle, H.A., Sweitzer, C.W., and Steffen, H.C., "Application of Very Fine Furnace Black in Low Temperature GR-S", Rubber Age (N.Y.), 64, 708 (1949)

Braendle, H.A., Estelow, R.K., and Wiegand, W.B., "Carbon Black Gel as a Factor in Natural Rubber Reinforcement", Rubber Age (N.Y. 65, 520 (1950)

Braendle, H.A., Steffen, H.C., and Sheppard, J.R., "Carbon pH and Structure in Rubber Compounding", India Rubber World, 113, 57 (1948)

Braendle, H.A., "The Comparative Behavior of Carbon Black in the Reinforcement of Natural and Synthetic Rubbers", Colloid Chem., 6, 408 (1946)

Brown,Jr., O.J., "Relation of Paint Properties to Surface Area of Carbon Black", Ind. Eng. Chem., 34, 352 (1942)

Clark, G.L., "Practical Evaluation of Commercial Rubber Carbon Blacks by X-ray Diffraction", Ind. Eng. Chem., Anal. Ed., 12, 66 (1940)

Cohan, L.H., "Carbon Black in All-Reclaim Tire Treads", India Rubber World, 112, 469 (1943)

Cohan, L.H., "Replacement of Easy Processing Channel Black with Medium Processing Channel and Semi-Reinforcing Black", Rubber Age (N.Y.), 52, 263 (1944)

Cohan, L.H., and Mackey, J.F., "Properties of Carbon Black", Ind. Eng. Chem., 35, 806 (1943)

Cohan, L.H., and Steinberg, M., "Conductivity of Tread Stocks - Natural and Synthetic Rubbers", Ind. Eng. Chem., 36, 7 (1944)

Cranor, D.F., "Broad Nomenclature for Carbon Blacks", India Rubber World, 112, 378 (1945)

Drogin, I., Grote, H.W., and Dillington, F.W., "Behavior of Carbon Blacks in Rubber", Ind. Eng. Chem., 36, 124 (1944)

Drogin, I., "A Study of Carbon Blacks in Natural and Synthetic Rubber", India Rubber World, 106, 561 (1942), 107, 42 (1942)

Drogin, I., "A Study of Carbon Blacks in Natural and Various Synthetic Rubbers", Rubber Age (N.Y.), 51, 483 (1942)

Drogin, I., "A Study of Carbon Black in Natural and Synthetic Rubbers", India Rubber World, 107, 42 (1942)

Emmett, P.H., "Measurement of Surface Area of Carbon Black by Low Temperature Adsorption", India Rubber World, 112, 270 (1943)

Falney, P., "Carbon Black Fire Hazard", India Rubber World, 103, 39 (Dec., 1940)

Garvey, B.S., and Freeze, J.A., "Effect of Carbon Blacks in Synthetic Tire Compounds", Ind. Eng. Chem., 34, 1277 (1942)

Garvey, B.S., and Freeze, J.A., "A Comparison of Carbon Black Groups in a GR-S Compound", Bulletin from Office of the United States Rubber Director, Washington, D.C., Aug. 7, 1943

Gehman, S.O., "X-ray Structure of Rubber - Carbon Black Mixtures", Ind. Eng. Chem., 32, 1401 (1940)

Goodwin, N., and Park, C.R., "Carbon Blacks and Their Uses in Rubber", Ind. Eng. Chem., 20, 621 (1928)

Grenquist, E.A., "Dispersion of Pigments in Rubber", Ind. Eng. Chem., 20, 1073 (1928), 21, 665 (1929)

Haynes, C.R., "Colloidal Carbon Compounding for Conservation", India Rubber World, 105, 478 (1942)

Heering, H., "Carbon Black Studies with the Electron Microscope", Metallurgical Eng., 49, 180 (1942)

Johnson, C.R., "Carbon Black; A Study of Its Volatile Constituents", Ind. Eng. Chem., 20, 904 (1928)

Johnson, C.R., "Carbon Black; The Role of Oxygen", Ind. Eng. Chem., 21, 1288 (1929)

Johnson, C.R., "Low Heat Generation Channel Carbon Black for Military Tires", India Rubber World, 105, 257 (June, 1942)

Kearsly, E.P.W., "Influence of Physical Properties of Carbon Black on Its Tinting Strength", Ind. Eng. Chem., 23, 835 (1931)

Ladd, W.A., and Wiegand, W.B., "Electron Microscope Studies of Colloidal Carbon Reticulate Chain Structure", Rubber Age (N.Y.), 53, 299 (1945)

Lewis, G.C., and Mantell, C.L., "Industrial Carbon", 2nd. Ed., D. Van Nostrand Company, Inc., New York, 1945

Lott, F.S., and Backus, H., "Carbon Black", Bureau of Mines Minerals Yearbook, Dept. of Interior, Washington, D.C., 1943, 1944

Parkinson, D., "Effect of Diameter and Surface Area of Carbon Black Particles On Certain Properties of Rubber Compounds", Trans. Inst. Rubber Ind., 19, 131 (1943)

Parinson, D., "Carbon Black in Rubber Compounding", Trans. Inst. Rubber Ind., 16, 87 (1940)

Pidgeon, L.M., "Properties and Recovery of Carbon Black in Luminous Flames", Can. Chem. and Met., 21, 240 (1937)

Plummer, W.B., "Abrasion Tests of Rubber Stocks Containing Various Types of Carbon Black", Ind. Eng. Chem., 20, 895 (1928)

Rehner, Jr., J., "Theory of Filler Reinforcement in Natural and Synthetic Rubber; the Stresses In and About the Particles, J. App. Phys., 14, 638 (1943)

Schoenfeld, F.K., "Surface Chemistry of Carbon Black", Ind. Eng. Chem., 27, 571 (1935)

Smith, W.R., "Surface Area and Properties of Carbon Black", Ind. Eng. Chem., 33, 1303 (1941)

Smith, W.R., "Thermal Conductivity of Carbon Blacks", Ind. Eng. Chem., 36, 1111 (1944)

Street, J.N., "Grit in Carbon Black - Effect on Flexing Resistance of Vulcanized Rubber", Ind. Eng. Chem., 34, 218 (1942)

Sweitzer, C.W., Goodrich, W.C., and Burgess, K.A., "The Carbon Black Gel Complex in Cold Rubber Reinforcement", Rubber Age (N.Y. 64, 629 (1949)

Sweitzer, C.W., and Goodrich, W.C., "The Carbon Spectrum for the Rubber Compounder", Rubber Age (N.Y.), 52, 469 (1944)

Thornhill, F.S., "Effect of Reinforcing Pigments on Rubber Hydrocarbon", Ind. Eng. Chem., 34, 218 (1942)

Turner, L.B., Haworth, J.P., Smith, W.C., and Zapp, R.L., "Carbon Black in Butyl Rubber", Ind. Eng. Chem., 35, 958 (1943)

White, L.M., Ebers, E.S., Shriver, G.E., and Buck, S., "Gel as a Definitive Property in GR-S Technology", Ind. Eng. Chem., 37, 770 (1945)

White, A.H. and Germer, L.H., "The Structure of Carbon Black", Chem. Phys., 9, 492 (1941)

Wiegand, W.B., "pH Properties of Colloidal Carbon", Ind. Eng. Chem., 29, 953 (1937)

Wiegand, W.B., "Some Properties of Carbon Black; Adsorption", Ind. Eng. Chem., 23, 646 (1931), 26, 413 (1934)

Wiegand, W.B. and Boggs, C.R., "Carbon Black in Rubber Insulating Compounds", Ind. Eng. Chem., 22, 822 (1930)

Wiegand, W.B., "Further Electron Microscope Studies of Colloidal Carbon and Role of Surface in Rubber Reinforcement", Can. Chem. Proc. Ind., 25, 579 (1941)

Wiegand, W.B., "Recent Developments in Colloidal Carbon", Can. Chem. Proc. Ind., 28, 3, 151 (1944)

Wiegand, W.B. and Ladd, W.A., "Colloidal Carbons as Revealed by the Electron Microscope", Rubber Age (N.Y.), 50, 431 (1942)

Win, H., Shelton, J.R., and Turnbull, D., "Role of Carbon Black in Oxidation of GR-S Vulcanizates", Ind. Eng. Chem., 38, 1052 (1946)

Zapp, R.L., "Reinforcement of Butyl Rubber; Role of Carbon Black Surface Chemistry", Ind. Eng. Chem., 36, 128 (1944)

(2) Manufacture of Carbon Black

Allen, R.G., "History, Use and Manufacture of Carbon Black", Refiner, 12, 384 (1935)

Anonymous, "Some Notes on Carbon Black", American Gas Journal, 15, 49 (Feb., 1930)

Anonymous, "Increasing Production of Carbon Black from Natural Gas", Franklin Institute Journal, 125 (Jan., 1930)

Anonymous, "Pressure Process Uses Less Gas to Make Carbon Black", Oil and Gas Journal, 30, 114 (2 April, 1931)

Anonymous, "Seeking to Increase Yield of Carbon Black", Oil and Gas Journal, 29, 96 (24 April, 1930)

Anonymous, "Factors Affecting Yield of Carbon Black", Oil News, 26 (Dec., 1922)

Anonymous, "More Uniform Production Claimed for Carbon Black; Isothermal Control", Rubber Age, (N.Y.), 50, 291 (1942)

Anonymous, "Carbon Black Makes a Start in Alberta", Can. Chem. Proc. Ind., 22, 335 (1938)

Anonymous, "Carbon Blacks - Their Manufacture and Use in Industry", Chem. & Ind., 354 (1946)

Anonymous, "Manufacture and Uses of Carbon Black", Pet. Times, 50, 898 (1927)

Bowles, C.E., "Increase Carbon Yield by Injection into Coke", Oil and Gas Journal, 29, 102 (22 May, 1930)

Cabot, T.D., "Origin and Development of the Carbon Black Industry", Oil and Gas Journal, 26, 68, 96, 98, 102 (13 Oct., 1927)

Cabot, T.D., "Some Aspects of Operation of Carbon Black Plants", Petroleum Engineer, 2, 202 (1930)

Cadman, W.H., "Colloidal Carbon", Engineering, 162,54 (1946)

Campbell, A.W., "Manufacture, Properties and Uses of Carbon Black", Rubber Age (N.Y.), 50, 21 (Oct., 1941)

Carson, C.M., "Some Observations on Carbon Black", Ind. Eng. Chem., 21, 911 (1929)

Chatfield, J.C., "Burner Control at Monroe Carbon Black Plants Increases Efficiency", Nat. Pet. News, 18, 59 (16 June, 1926)

Chamberlin, D.S. and Rose, A., "A Study of the Factors Involved in the Formation of Carbon Black from Natural Gas", Trans. Am. Inst. Chem. Eng., 22, 155 (1929)

Crowe, J.M., "Carbon Black Process; Continental Carbon Co.", Chem. Ind., 50, 64 (Jan., 1942)

Dewey, C.S., "Technical Aspects of Carbon Black Manufacture", Pet. Eng., 2, 128, 130, 132 (Sept., 1930)

Drogin, I., "Commercial Processes for Carbon Black", India Rubber J., 110, 259 (1935)

Drogin, I., "Development and Status of Carbon Black", United Carbon Co. Inc., Charleston, W. Virginia, 1945

Ellis, Carleton, "Carbon Black Manufacture", In Dunstan, A.E., The Science of Petroleum, vol. 4, 1928, p. 2851-2855

Ford, R., "Natural Gas, Flames and Carbon Black", Gas Age, 28, 26 (11 March, 1943)

Francis, A.W., "The Flame-Pressure Process for Carbon Black", Ind. Eng. Chem., 23, 612 (1931)

Fuchs, H., "Development of the German Ersatz for Carbon Black", India Rubber World, 105, 147 (Nov., 1941)

Gallie, J.F., "Carbon Black", Pet. Ref., 23, 93, (1944), 23, 97 (1944)

Gallie, J.F., "Carbon Black Manufacture", Pet. Proc., 1, 197 (Nov., 1946)

Gordon, A.S., "Pyrolysis of Methane in a Porcelain Tube", J. Am. Chem. Soc., 70, 395 (1948)

Haynes, C.R., "Bead Process Gives Clean Carbon Black", Chem. Met. Eng., 45, 187 (April, 1938)

Jakosky, J.J., "Electrical Manufacture of Carbon Black", In U.S. Bureau of Mines Technical Paper No. 351, 1924

Jakosky, J.J., "The Production of Carbon Black from Natural Gas by the High Voltage Arc", Oil and Gas Journal, 22, 76 (20 Sept.1923)

Johnson, C.R., "Isothermal Control of Channel Carbon Black Production", India Rubber World, 105, 367 (Jan., 1942)

Kassel, L.S., "Thermal Decomposition of Methane", J. Am. Chem. Soc., 54, 3949 (1932)

Kirk, R.E. and Othmer, D.F., "Carbon Black", Encyclopedia of Chemical Technology, Vol 3, p. 52, The Interscience Encyclopedia Inc., New York, 1947

Kaufman, C., "Acetylene Carbon Black", Can. Chem. Met., 17, 93 (1933)

Kauffman, H.L., "Progress in Carbon Black Manufacture", Oil Weekly, 5, 31, 71 (9 Aug., 1929)

Linz, C.L., "Electrical Process Makes Carbon Black from Distillates", Refiner, 8, 29, 32 (Sept., 1925)

Loving, W.L., "Carbon Black", Pet. Eng., 17, 176 (Nov., 1945)

Moore, R.L., "Thermatomic Process for Cracking of Gaseous Hydrocarbons", Ind. Eng. Chem., 24, 21 (1932)

Moses, Leslie, "Review of Statutory Regulations in the Carbon Black Industry", Oil and Gas Journal, 41, 30 (9 April, 1942)

Neal, R.O. and Perrott, G. St.J., "Carbon Black - Its Manufacture, Properties and Uses", Bureau of Mines Bulletin, Number 1932, Department of the Interior, Washington, D.C., 1922

Neal, R.O., "Manufacture of Carbon Black from Natural Gas", In U.S. Bureau of Mines Report of Investigation, No. 2091, 1920

Nelson, W.L., "Furnace Black for Synthetic Rubber", Oil and Gas Journal, 42, 62 (11 March, 1943)

Odell, Wm. W., "Cracking Natural Gas in Water-Gas Generators with Recovery of Carbon Black", In U.S. Bureau of Mines Report of Investigation, No. 2991, March, 1930.

Parkinson, D., "Role of Carbon Black in Rubber Manufacture", Chemistry and Industry, 36, 325 (1944)

Pettyjohn, E.S., "Germany Made Acetylene and Carbon Black by Cracking Natural Gas in Electric Arc", Nat. Pet. News, 38, R596 (1946)

Pidgeon, L.M., "A New Process for the Manufacture of Carbon Black by Thermal Decomposition of Hydrocarbon Gases", Canadian Journal of Research, B 13, 351 (1935)

Pidgeon, L.M., "The Channel Process - Production from the Natural Gas of Turner Valley, Alberta", Canadian Journal of Research, B 14, 127 (1936)

Pidgeon, L.M., "The Channel Process - Production from Pyrolysis Waste Gases", Canadian Journal of Research, B 15, 139 (1937)

Plummer, W.B., "Production of Carbon Black from Propane", Ind. Eng. Chem., 22, 1209 (1930)

Reid, George, "Development in the Carbon Black Industry", Refiner, 14, 148, 152 (March, 1931), 14, 117, 120, 122, 124 (April, 1931)

Rice, F.O., "Free Radicals in Thermal Decomposition", J. Am. Chem. Soc., 53, 1959 (1931)

Rongone, R.L., "Incorporation of Carbon Black into GR-S Latex (On a Production Scale), Rubber Age (N.Y.), 59, 577 (1944)

Slater, W.E., "Influence of Various Surfaces on the Decomposition of Methane", J. Chem. Soc., 109, 160 (1916)

Stokes, C.A. and Dobbin, R.E., "Carbon Black Shifts to the Furnace Process", Chem. Ind., 64, 40 (1949)

Stokes, C.A. and Dannenberg, E.M., "Carbon Blacks", Ind. Eng. Chem., 41, 381 (1949)

Storch, H.H., "Thermal Decomposition of Methane by a Carbon Filament", J. Am. Chem. Soc., 54, 4188 (1932)

Wiegand, W.B., "Notes on the Carbon Black Flame", Ind. Eng. Chem., 23, 178 (1931)

(3) Economics

Anonymous, "Natural Gas, Carbon Black and Gasoline Expansion", Oil and Gas Journal, 35, 68 (15 Oct., 1936)

Anonymous, "Texas Panhandle - The Center of the Carbon Black Industry", Pet. Eng., 4, 126 (Sept., 1932)

Anonymous, "Great Carbon Black Industry", American Gas Journal, 33 (May, 1944)

Anonymous, "Furnace Blacks - Present and Future", India Rubber World, 116, 361, 412 (1947)

Anonymous, "Carbon Black and Its Relations to the Natural Gas Industry", Interstate Oil Compact Quarterly Bulletin, Oklahoma City, Oklahoma (1945)

Bredberg, L.E., "Carbon Black Overproduction New Threat in Permian Basin", Oil and Gas Journal, 29, 102 (22 May, 1930)

Carr, R.L., "Carbon Black - A Vital Business Need", Oil and Gas Journal, 25, G-198, G-200, G-202, (16 June, 1927)

Cohan, L.H., "Carbon Black in War and Peace", Chem. and Eng. News, 2078 (1945)

Crowell, A.M., "Natural Gas Carbon Black and Natural Gasoline Industries in State of Texas", Oil and Gas Journal, 36, 78 (14 April, 1938)

Gallie, J.F., "Carbon Black", Pet. Ref., 23, 115 (1949)

Hopkins, G.R., "Some Economic Phases of the Carbon Black Industry", In U.S. Bureau of Mines Information Circular No. 6033, 1944

Miller, B., "Changing Economics of Carbon Black Manufacture", Chem. Ind., 56, 786 (1945)

Reardon, W.E., "The Natural Gasoline Situation from the Standpoints of Natural Gas Pipeline and Carbon Black Manufacture", In Natural Gasoline Association of America, Proceedings of 10th Annual Convention, 1931, p. 19

Reardon, W.E., "Operations of Pipelines and Carbon Black Plants Related", Oil and Gas Journal, 30, 141, 150 (21 May, 1931)

Reed, Paul, "Texas Panhandle - Center of Carbon Black Industry", Oil and Gas Journal, 37, 12 (1 Sept., 1938)

Ross, W.A., "How the Carbon Black Industry Succeeds in Making Profit from Tail Gas", Pet. Eng., 2, 86 (April 1930)

B29763